

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number
WO 01/28502 A1

(51) International Patent Classification⁷: **A61K 7/00**

(21) International Application Number: **PCT/EP00/10378**

(22) International Filing Date: 19 October 2000 (19.10.2000)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/425,366 22 October 1999 (22.10.1999) US
09/425,717 22 October 1999 (22.10.1999) US

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for all designated States except AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, IN, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors: **NASER, Mark, Stephen**; Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020 (US). **VASUDEVAN, Tirucherai, Varahan**; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). **ROSANO, Henri, Louis**;

848 Woodland Avenue, Oradell, NJ 07649 (US). **GANDOLFO, Francois, Gerard**; 712 60th Street, Brooklyn, NY 11220 (US). **MOUNCINE, Kanouni**; 216 W 100th Street, New York, NY 10025 (US).

(74) Agent: **ROTS, Maria, Johanna, Francisca**; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/28502 A1

(54) Title: **STABLE MULTIPLE EMULSION COMPOSITION**

(57) Abstract: W₁-O-W₂ emulsions are disclosed in which the W₁/O emulsion comprises an internal aqueous phase comprising a benefit agent and an oil phase surrounding it, and, around this is found an external isotropic aqueous phase wherein the external surfactant phase does not comprise an amido containing anionic. Methods of stabilizing the multiple oil compositions are also disclosed.

- 1 -

STABLE MULTIPLE EMULSION COMPOSITIONFIELD OF THE INVENTION

5 The present invention relates to liquid surfactant compositions, e.g., liquid shower gels or liquid shampoos, comprising multiple emulsions. In particular, the invention relates to multiple emulsion compositions which may comprise high levels of surfactants but are nonetheless stable (e.g.,
10 microscopically stable). In another embodiment, the compositions microscopically maintain multiple emulsion droplet integrity while, macroscopically, there is little or no phase separation. The invention also relates to methods of stabilizing the multiple emulsion compositions.

15

BACKGROUND OF THE INVENTION

Multiple emulsion systems (broadly defined as systems in which water/oil and oil/water emulsion co-exist) are very valuable
20 because they permit incorporation and enhanced delivery of benefit agents. Thus, multiple emulsions have been used for many years, for example, in cosmetic and pharmaceutical areas to deliver cosmetic or pharmacological benefit agents (see for Example, U.S. Patent No. 5,306,498 to Vesperini; or U.S.
25 Patent No. 5,567,426 to Nadaud et al.).

In general, however, as the level of cleansing surfactant (e.g., having high HLB, e.g., HLB greater than 10, preferably greater than 12) in such multiple emulsion
30 systems is increased, the emulsions become less and less stable. Thus, for example, the level of cleansing

- 2 -

surfactant in almost all of the cosmetic and pharmaceutical compositions referred to in the prior art is below 5% by wt. of the compositions. Greater amounts lead to less stability and phase separation.

5

U.S. Patent Nos. 5,656,280 and 5,589,177 (Herb *et al.*) and their European equivalents EP 717,978 and EP 715,842 describe the stabilization of multiple emulsions in compositions containing high levels of conditioning
10 surfactant. However, the stable multiple emulsion composition disclosed therein comprise surfactants (i.e., conditioning surfactants) which must form stabilizing liquid crystals, i.e., lamellar liquid crystals. The compositions described wherein the surfactants formed an isotropic phase
15 (for example, Example 29 at column 29 of U.S. Patent No. 5,589,177 at lines 30-44) were unstable (see column 34, where stability of Example 29 is only 5 minutes). The applicants have now surprisingly found that the surfactant phase of compositions of the present invention is an
20 isotropic surfactant phase, yet the multiple emulsion does not break into a simple emulsion when evaluated at room temperature for at least 2 weeks, preferably greater than 4 weeks, more preferably greater than 8 weeks, when measured at a temperature of about 25°C.

25

Compositions comprising isotropic surfactant phases are advantageous over compositions comprising lamellar liquid crystal phase in that they can be formed using a much wider range of surfactants and provide improved foam/lather
30 properties.

- 3 -

Accordingly, it is an object of the invention to provide compositions with a surfactant phase which is not limited to lamellar phase.

- 5 It is another object of the invention to provide a surfactant phase (which is an isotropic phase) which contains high levels of surfactant and yet does not destabilize the multiple emulsion.
- 10 In a second embodiment, it has been further found that compositions may be stabilised over time (in addition to being microscopically stable as noted) by using specific selection of an external surfactant system in combination with a stabilizing natural gum polymer which forms a gelled
- 15 external aqueous phase with a relatively high concentration of surfactant. Compositions which employ similar technology (i.e. gelled external aqueous phase) are described in U.S. Patent No. 5,306,498 to Vesperini, U.S. Patent No. 4,083,798 to Versteeg, U.S. Patent No. 5,332,595 to Gaonkar,
- 20 U.S. Patent Nos. 5,576,064 and 5,656,263 both to Fructus, and U.S. Patent No. 5,567,426 to Nadaud. In the prior art compositions disclosed, however, the level of high HLB external surfactant was in one case only 5% and in most cases zero.
- 25
- It is thus yet another object of this invention to provide a gelled isotropic external surfactant phase which contains high levels of surfactant where the integrity of the multiple emulsion droplet is maintained and the composition
- 30 does not phase separate.

- 4 -

BRIEF SUMMARY OF THE INVENTION

In one embodiment, applicants have now found that it is possible to obtain multiple emulsion systems which comprise high levels of surfactant forming an isotropic phase whereby the multiple emulsion can deliver desirable benefit agent (e.g., in the internal oil phase) while simultaneously maintaining the stability of the multiple emulsion. Previously it has been difficult or impossible to make stable multiple emulsions in the presence of high levels of surfactant which form an isotropic phase. In preferred embodiments, the surfactant system comprises mixtures of anionic and amphoteric surfactants and levels of surfactant are greater than about 10.5% by wt. of the total composition.

The invention further relates to methods of stabilizing the multiple emulsion systems described above.

More specifically, the invention comprises a water-in-oil-in-water (W_1 -O- W_2) multiple emulsion wherein the water-in-oil (W_1 /O) emulsion itself comprises an internal aqueous phase (W_1) which contains a solute and optional surfactant; an oil phase O (an oil combined with a low HLB emulsifier, e.g., emulsifier with HLB less than 10) surrounding the internal aqueous phase; and a topically active compound which may be in either the aqueous W_1 or in O. The W_1 O phase is surrounded by an external aqueous isotropic phase (W_2) containing cleansing surfactant, optional topically active

- 5 -

compound (which may be the same or different as the first optional topically active compound), and optional solute. (It should be understood that some solute will almost always be present in the surfactant or will be formed when
5 adjusting pH). It is critical that the surfactant phase W_2 must not contain an anionic surfactant with an amido group.

Another essential feature is that the oil in the O phase should not comprise more than 50% unsaturated compounds; or
10 should not be a volatile silicone (e.g., a silicone having a viscosity of 10 centistokes or less).

As noted above, the invention may be distinguished from the prior art (for example U.S. Patent No. 5,656,280) which
15 requires that the aqueous phase W_2 (e.g., external aqueous phase) comprises a surfactant system capable of forming stabilizing liquid crystals. In contrast, the present application requires that the external aqueous phase be an isotropic phase. The isotropic phase in turn is formed by
20 selection of a specific surfactant system which must not contain an anionic surfactant with an amido group.

By definition, a lamellar phase is a liquid crystalline phase whereas an isotropic phase is micellar; optically a
25 lamellar phase would show birefringence under a polarized light source while a micellar phase does not exhibit this feature.

In particular, the invention comprises a W_1 -O- W_2 multiple
30 emulsion composition comprising:

- 6 -

(1) about 1% to 99% by wt. of the composition, preferably 2% to 90% by wt., more preferably 5% to 80% of a W₁/O emulsion comprising;

5 (a) about 1% to 99% of the emulsion of an internal aqueous phase comprising (i) water; (ii) 0.01 to 30% solute; and (iii) 0 to 30% optional surfactant;

10 (b) about 0.1% to about 99%, preferably 0.5 to 95%, more preferably 1 to 80% of the emulsion of an oil phase surrounding the internal aqueous phase comprising a non-volatile silicone compound, a volatile hydrocarbon compound, a non-volatile hydrocarbon compound or a mixture thereof;

15 (c) about 0.1 to 20%, preferably 1 to 15%, more preferably 1.5 to 15% by wt. emulsion of a surfactant emulsifier selected from a silicon-free surfactant or surfactant blend having an HLB value of about ten or less, an oil soluble silicon based
20 surfactant, an oil-soluble polymeric surfactant and mixtures thereof; and

(d) a topically effective amount (e.g., 0.01 to 40%, preferably 0.05 to 15% by wt.) of a first topically active compound which may be found in
25 either aqueous phase (a) and/or oil phase (b); and

(2) about 1 to 99% by wt., preferably 20 to 95% by wt. of an external isotropic aqueous phase W₂ comprising non-amido anionic and/or other
30 surfactants. Preferably the composition contains non-amido anionic and amphoteric surfactants,

- 7 -

wherein the ratio of first surfactant (preferably anionic) to amphoteric is 100:1 to 1:100. The composition optionally contains a second topically effective compound, typically 0-40% by wt. of the external phase to perform a function identical to, similar to or different from the first topically active compound, and optional solute. The surfactant will typically comprise about 2-80% of the aqueous phase.

10

The W_1 -O- W_2 multiple emulsion compositions are stable (e.g., typically they will not break down into a simple emulsion at room temperature for at least two weeks) and they exhibit exceptional aesthetic and functional properties. The W_1 -O-

15 W_2 multiple emulsion compositions are liquids or creams, and are capable of effectively delivering one or more topically active compounds to the skin or hair from a single composition.

20 In a second embodiment, applicants have now found that specific selection of an external surfactant system in combination with a stabilizing natural gum polymer which forms a gelled external aqueous phase with a relatively high concentration of surfactant, results in the formation of a multiple emulsion system which enables delivery of desirable benefit agent(s) while simultaneously maintaining both the integrity of the multiple emulsion droplets and physical stability of the composition (i.e. the bottom clear layer formed due to phase separation should be less

- 8 -

than 20 volume percent of the total volume of the sample for a period of at least 45 days at room temperature.)

Specifically, this embodiment relates to the selection of
5 natural gum polymers and surfactant(s) or combinations of surfactants which form a gelled external phase for the multiple emulsions described above.

The invention, therefore, further comprises a W_1 -O- W_2
10 multiple emulsion wherein the W_1 O phase, in addition to being surrounded by an external aqueous isotropic phase W_2 , an optional topically active compound and an optional solute, is also surrounded by a stabilizing natural gum polymer.

15

It is essential that the natural gum stabilizer and the selected surfactant(s) form a gel. As in the first embodiment, it is also essential that the surfactant phase W_2 must not contain an anionic surfactant with an amido
20 group. Furthermore, the W_2 surfactant phase must be isotropic. The isotropic phase in turn is formed by selection of a specific surfactant system which must not contain an anionic surfactant with an amido group.

25 The oil in the O phase (e.g., light mineral oil, hexadecane, octyl palmitate) should preferably not comprise (1) more than 50% unsaturated compounds; or (2) should not be a volatile silicone (e.g., a silicone having viscosity of 10 centistokes or less).

- 9 -

As noted above, the invention can be distinguished from prior art U.S. Patent Nos. 5,306,498 (Vesperini) 4,083,798 (Versteeg) 5,332,595 (Gaonkar), 5,576,064 and 5,656,263 (Fructus), and 5,567,426 (Nadaud) because our invention uses surfactant levels of 10.5% or greater whereas the aforementioned compositions use levels of only 0-5% external surfactant.

10 In particular, the invention further comprises a W_1 -O- W_2 multiple emulsion composition comprising:

(1) about 1% to 99% by wt. of the composition, preferably 2% to 90% by wt., more preferably 5% to 80%, more preferably 5 to 50% of a W_1 /O emulsion comprising;

(a) about 1% to 99% of the emulsion of an internal aqueous phase comprising (i) water; (ii) 0.01 to 30% solute; and (iii) optional 0 to 30% surfactant;

(b) about 0.5% to about 99%, preferably 1 to 80% of the emulsion of an oil phase surrounding the internal aqueous phase comprising a non-volatile silicone compound, a volatile hydrocarbon compound, a non-volatile hydrocarbon compound or a mixture thereof;

(c) about 0.1 to 20%, preferably 1 to 15%, more preferably 1.5 to 15% 1.5 to 15% by wt. emulsion of a surfactant emulsifier selected from a silicon-free surfactant or surfactant blend having an HLB value of about ten or less, an oil soluble

- 10 -

silicon based surfactant, an oil-soluble polymeric surfactant and mixtures thereof; and

(d) a topically effective amount (e.g., 0.01 to 40%, preferably 0.05 to 15% by wt.) of a first topically active compound which may be found in either aqueous phase (a) and/or oil phase (b); and

(2) about 1 to 99% by wt., preferably 20 to 95% by wt. of an external isotropic aqueous phase W_2 comprising non-amido anionic and/or other surfactants.

The composition contains all non-amido anionic or all amphoteric surfactant, or combinations of the two in which 60% by weight or greater is the anionic surfactant. The surfactant typically comprises about 2-80% of the aqueous phase and 0.01 to 10% of a stabilizing natural gum polymer.

The composition optionally contains a second topically effective compound, typically 0-40% by wt. of the external phase to perform a function identical to, similar to or different from the first topically active compound and optional solute. It is preferred that in systems where the external surfactant W_2 is comprised entirely of, or contains a majority of, anionic surfactant, that a nonionic gum polymer is used. Conversely, in systems where the external surfactant W_2 is comprised entirely of or contains a majority of amphoteric surfactant, it is preferred that an anionic gum polymer is used.

30

- 11 -

The W_1 -O- W_2 multiple emulsion compositions are physically stable (e.g., typically they will not phase separate at room temperature for at least 45 days and exhibit exceptional aesthetic and functional properties. The W_1 -O- W_2 multiple emulsion compositions are liquids or creams, and are capable of effectively delivering one or more topically active compounds to the skin or hair from a single composition.

BRIEF DESCRIPTION OF THE FIGURES

10

Figure 1 relating to a first embodiment of invention is a schematic drawing wherein Figure 1A shows a stable multiple emulsion in which the W_1 /O phase is surrounded by the W_2 phase and Figure 1B shows a multiple emulsion which has broken down into a simple O/(W_1 + W_2) emulsion.

Figures 2 and 3 relating to a second embodiment of the invention both show a plot of viscosity vs Haake RV06 spindle speed. In Figure 2, it is clear that the addition of 3% by weight of an anionic natural gum (example carrageenan) to an amphoteric surfactant (example cocamidopropyl betaine) yields a gelled external W_2 phase i.e. a viscoelastic solution that exhibits shear thinning behavior. In Figure 3, it is clear that the addition of 1% by weight of a nonionic natural gum (example locust bean) to an anionic surfactant (example sodium laureth sulfate) yields a gelled external W_2 phase. In each of these cases, addition of the gum to the surfactant has transformed the rheology of the W_2 phase from a Newtonian low viscosity to a shear thinning, high viscosity gel. This gelled external

- 12 -

(W2) phase, resulting from proper surfactant and stabilizer selection, helps keep the multiple emulsion from phase separating while still rendering the composition pourable. A viscosity of at least 6000 cps at a spindle speed of 5 rpm and a viscosity of no more than 9000 cps at 50 rpm are preferred to render the composition phase both stable and pourable.

DETAILED DESCRIPTION OF THE INVENTION

10

In a first embodiment, the present invention relates to W_1 -O- W_2 multiple emulsion compositions comprising:

- (1) 1 to 99% W_1 /O emulsion comprising about 1% to 99% of W_1 (containing water, solute and optional surfactant), and 0.1 to 99% of O phase (containing oil compound and low HLB emulsifier). A topically active agent may be present in W_1 phase, O phase or both; and
- (2) about 1% to 99% by wt. of an external aqueous phase comprising non-amido anionic and/or other surfactants. The phase preferably comprises anionic, amphoteric, optional second topically effective compound, and solute.

The external aqueous phase W_2 (1 to 99% of total emulsion) differs from the art in that it is an isotropic, aqueous surfactant phase rather than a lamellar phase. These

- 13 -

compositions are able to comprise relatively large amounts of surfactants (i.e., 10.5% by wt. or greater, preferably 11% -75%, more preferably 12% to 60%, more preferably 13% to 60%, more preferably 15% to 60%, more preferably 16% to 55%,
5 more preferably 17 to 50% by wt. of the composition) while the integrity of the multiple emulsion still remains. Unless the surfactant system and oil are specifically selected as described herein, such multiple emulsion compositions will generally break very rapidly into simple
10 emulsion (see Figure 1).

In a second embodiment, the invention relates to W_1 -O- W_2 multiple emulsions where the integrity of the multiple emulsion droplet is maintained and the composition does not
15 phase separate. These formulations comprise:

- (1) 1 to 99% W_1 /O emulsion comprising about 1% to 99% of W_1 (containing water, solute and optional surfactant), and 0.5 to 99% of O phase (containing
20 oil compound and low HLB emulsifier). A topically active agent may be present in W_1 phase, O phase or both; and
- (2) about 1% to 99% by wt. of an external aqueous phase
25 comprising non-amido anionic and/or amphoteric surfactant, a stabilizing natural gum polymer, an optional second topically effective compound, and solute.

- 14 -

The external aqueous phase W2 contains a high concentration (i.e., 15% by wt. or greater, preferably 16% or greater, preferably 17 to 75%, more preferably 20 to 70%, more preferably 22% to 60%, more preferably 25 to 50% by wt. of the composition) of surfactant which is isotropic. It is essential that the natural gum stabilizer and the selected surfactant(s) form a gel. Applicants have unexpectedly found that in systems where the external surfactant W2 is comprised entirely of or contains a majority of anionic surfactant, that a nonionic gum polymer should be used. Conversely, in systems where the external surfactant W2 is comprised entirely of or contains a majority of amphoteric surfactant, that an anionic gum polymer should be used. This differs from prior art in that the external phase now contains high levels of cleansing surfactant and the choice of stabilizing polymer is subject to the above criticalities.

The invention will now be described in greater detail.

The Water-in-Oil (W_1/O) Emulsion

The W_1/O emulsion comprises an internal aqueous phase W_1 with water, solute and optional surfactant, and an oil phase O.

Generally the water, solute and first topically-active compound comprise the internal aqueous phase of the W_1/O emulsion although the active compound may also be in the oil phase if oil compatible. That is, the W_1 phase comprises

- 15 -

droplets containing water, solute and possibly a first topically-active compound. For example, droplets containing water, solute and a first topically-active compound (W_1) may have a diameter ranging from about 0.01 to about 75 and may be enveloped by a membrane or film comprising the oil phase. The contents of the internal aqueous phase (W_1) therefore do not contact the external aqueous phase (W_2) of the W_1 -O- W_2 multiple emulsion.

10 The primary W_1 /O emulsion is present in a W_1 -O- W_2 multiple emulsion composition in an amount of about 1% to about 99%, preferably 2% to 90%, more preferably about 5% to about 80%, by weight of the multiple emulsion composition. Suitably, the primary W_1 /O emulsion is present in an amount of about 15 10% to about 80%.

The Internal Aqueous Phase

The (W_1) internal aqueous phase comprises about 1% to about 20 99% by weight of the emulsion, an oil phase separates the internal aqueous phase (W_1) of the emulsion from the external aqueous phase (W_2).

The internal aqueous phase (W_1) of the present W_1 -O- W_2 25 multiple emulsion compositions generally comprises water, solute and an optional first topically-active compound (which may also be found in the oil phase alone or in both). The internal aqueous phase may further comprise additional

- 16 -

topically-active compounds and/or optional water soluble compounds capable of providing a desired aesthetic or functional effect, such as a fragrance:

- 5 The aqueous phase (W_1) comprises about 1% to about 99%, and preferably about 10% to about 95%, more preferably about 25% to about 95% by weight of the W_1/O emulsion.

Topically-Active Compounds

10

A wide variety of topically active compounds may be incorporated into the W_1/O emulsion as the first topically active compound. If found in the W_1 phase, the topically active compounds are water soluble or water dispersible and
15 include both cosmetic and other compounds that act upon contact with the skin or hair. The first topically active compound is present in a sufficient amount to perform its intended function, typically in an amount of about 0.01% to about 40% by weight, preferably 0.05 to 15% of the W_1/O
20 emulsion.

The first topically active compound typically remains on the skin or hair after application, as opposed to being rinsed from the skin or hair. However, in some cases the first
25 topically active compounds are designed to be rinsed from the skin or hair after the compound has performed its intended function.

- 17 -

The first topically active compound may be incorporated into the aqueous phase or into the oil phase of the primary emulsion, or both. Whether a particular first topically active compound is incorporated into the aqueous phase or
5 the oil phase of the primary emulsion is related to the solubility of the topically active composition in water. In preferred embodiments, the first topically active compound is water soluble and is incorporated into the internal W_1 aqueous phase. However, a more hydrophobic agent may be
10 used in the oil phase.

As used herein, the term "water soluble" means water soluble or water dispersible. A water soluble compound has a water solubility of at least 0.1 g (grams) per 100 ml
15 (milliliters) of water and forms a true solution. A water soluble compound can be inherently water soluble or can be made water soluble by the addition of a solubilizing compound, such as a coupling agent, a co-surfactant, or a solvent. A water dispersible compound remains dispersed in
20 water for at least the time period necessary to manufacture the primary W_1/O emulsion, i.e., at least about one hour.

In addition, the topically active compound may be incorporated into the external aqueous phase W_2 to achieve
25 enhanced efficacy.

The topically active compound therefore can be one of, or a combination of, a cosmetic compound, a medicinally active compound or any other compound that is useful upon topical
30 application to the skin or hair. Such topically active

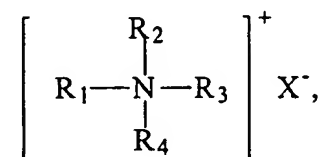
- 18 -

compounds include, but are not limited to, hair and skin conditioners, hair and skin cleansers, hair fixatives, hair dyes, hair growth promoters, deodorants, skin care compounds, permanent wave compounds, hair relaxers, hair
5 straighteners, antibacterial compounds, antifungal compounds, anti-inflammatory compounds, topical anaesthetics, sunscreens and other cosmetic and medicinal topically effective compounds.

10 In accordance with one aspect of the present invention, the topically active compound comprises a water soluble hair conditioner, such as a quaternary ammonium compound. Quaternary ammonium compounds are substantive to the hair and are excellent hair conditioners, but are well known to
15 be incompatible with anionic surfactants and anionic dyes. Therefore, quaternary ammonium compounds are generally not a component of shampoo conditioner compositions or anionic dye-based compositions, but are applied to the hair from a separate conditioning composition.

20

Water soluble quaternary ammonium compounds suitable for the purposes of the present application have the general structural formula:



25

wherein R_1 is an alkyl group containing from about 8 to about 18 carbon atoms; R_2 is selected from an alkyl group

- 19 -

containing from about 8 to about 18 carbon atoms, a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group and a hydroxyethyl group; R_3 is selected from a benzyl group, a hydrogen atom, an ethyl group, a methyl group, a hydroxymethyl group and a hydroxyethyl group; R_4 is selected from a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group and a hydroxyethyl group; and X is an anion. The quaternary nitrogen of the water soluble quaternary ammonium compound also can be a component of a heterocyclic nitrogen containing moiety, such as morpholine or pyridine. The anion of the quaternary ammonium compound can be any common anion, such as chloride, methosulfate, ethosulfate, nitrate, bromide tosylate, acetate, or phosphate.

15

The water soluble quaternary ammonium compounds may have one or two long chain alkyl groups containing from about 8 to about 18 carbon atoms. The long chain alkyl groups can also include, in addition to, or in replacement of, carbon and hydrogen atoms, either linkages or similar water solubilizing linkages. The remaining two or three substituents of the quaternary nitrogen of the quaternary ammonium compound can be hydrogen; or benzyl, or short chain alkyl or hydroxyalkyl groups, such as methyl, ethyl, hydroxymethyl or hydroxyethyl groups; or combinations thereof, either of the same or different identity.

Exemplary water soluble quaternary ammonium compounds include, but are not limited to laurtrimonium chloride; Quaternium-16; lauralkonium chloride; olealkonium chloride; dilauryldimonium chloride; cetalkonium chloride;

- 20 -

dicetyldimonium chloride; laurylpyridinium chloride;
cetylpyridinium chloride; soyatrimonium chloride;
Polyquaternium-6; Polyquaternium-7;
guarhydroxypropyltrimonium chloride; Polyquaternium-11;
5 Polyquaternium-5; Polyquaternium-10; Polyquaternium-24;
cetrimonium chloride; Quaternium-24; mytrimonium chloride;
PEG-2 cocomonium chloride; PEG-2 cocoyl quaternium-4; PEG-15
cocoyl quaternium-4; PEG-2 stearyl quaternium-4; PEG-2 oleyl
quaternium-4; and PEG 15 olelyl quaternium-4, and mixtures
10 thereof, wherein the compound designation is provided by the
Cosmetic, Toiletry and Fragrance Association, Inc. in the
CTFA Cosmetic Ingredient Dictionary, 4th Ed., 1991,
hereinafter referred to as the *CTFA Dictionary*. Other water
soluble quaternary ammonium compounds are listed in the *CTFA*
15 *Cosmetic Ingredient Handbook*, 1st Ed., 1988 (hereinafter the
CTFA Handbook) at pages 40-42, incorporated herein by
reference.

Other water soluble hair conditioners are also suitable as
20 the first topically active compound. Such hair conditioners
include, but are not limited to, fatty amine salts,
ethoxylated fatty amine salts, dimethicone copolyols,
protonated polyethylenimines, protonated ethoxylated
polyethylenimines, soluble animal collagen, lauramine oxide,
25 cationic polymers, numerous other water soluble hair
conditioners listed in the *CTFA Handbook* at page 71-73,
(incorporated herein by reference) and mixtures thereof.

In addition to hair conditioners, a skin conditioner can be
30 used as the first topically active compound. Skin
conditioning agents include, but are not limited to,

- 21 -

humectants, such as fructose, glucose, glycerin, propylene glycol, glycereth-26, mannitol and urea; pyrrolidone carboxylic acid; hydrolyzed lecithin; coco-betaine; cysteine hydrochloride; glutamine; PPG-15; sodium gluconate; potassium aspartate; oleyl betaine, thiamine hydroxychloride; sodium laureth sulfate; sodium hyaluronate; hydrolyzed proteins; hydrolyzed keratin; amino acids; amine oxides; water soluble derivatives of vitamins A, E and D; amino functional silicones; ethoxylated glycerin; alpha-hydroxy acids and salts thereof; water soluble fatty oil derivatives, such as PEG-24 hydrogenated lanolin, almond oil, grape seed oil and castor oil; numerous other water soluble skin conditioners listed in the *CTFA Handbook*, pages 79-84, (incorporated herein by reference); and mixtures thereof. Other conditioners include alpha hydroxy acids such as lactic acid, glycolic acid or their salts thereof.

The first topically active compound may also be a hair fixative or film former that imparts style retention properties to hair, i.e., sets the hair. The hair fixative typically is a homopolymer, a copolymer, or a terpolymer. The polymers can be nonionic, amphoteric, anionic or cationic. Examples of hair fixatives include, but are not limited to, an acrylamide copolymer; an acrylamide/sodium acrylate copolymer; a polystyrene sulfonate; a polyethylene oxide; a water dispersible polyester; a cationic cellulose; an acrylate/ammoniummethacrylate copolymer; an aminoethylacrylate phosphate/acrylate copolymer; a polyacrylamide; Polyquaternium-1; Polyquaternium-2; Polyquaternium-4; Polyquaternium-4; Polyquaternium-5; Polyquaternium-7; Polyquaternium-8; Polyquaternium-9;

- 22 -

Polyquaternium-10; Polyquaternium-11; Polyquaternium-12;
Polyquaternium-13; Polyquaternium-14; Polyquaternium-15;
Polyquaternium-16; Polyquaternium-28; a PVP
(polyvinylpyrrolidone); a PVP/
5 dimethylaminoethylmethacrylate copolymer; a PVP/ethyl
methacrylate/methacrylic acid copolymer; a carboxylated
polyvinyl acetate; vinyl/caprolactam/PVP/dimethylaminoethyl
methacrylate copolymer (GAFFIX VC713); a PVP/vinyl acetate
copolymer; a sodium acrylate/ vinyl alcohol copolymer;
10 sodium carrageenan; a vinyl acetate/crotonic acid copolymer;
numerous other water soluble hair fixatives listed in the
CTFA Handbook at pages 73-74, incorporated herein by
reference; and mixtures thereof. Numerous hair fixatives
also are disclosed in U.S. Patent No. 5,277,899,
15 incorporated herein by reference.

The first topically active compound may also be a water
soluble hair dye, such as, but not limited to, m-aminophenol
hydrochloride, p-aminophenol sulfate, 2,3-diaminophenol
20 hydrochloride, 1,5-naphthalenediol, phenylenediamine
hydrochloride, sodium picramate, water soluble cationic
dyes, water soluble anionic dyes, water soluble FD&C dyes,
such as Blue No. 1, Blue No. 2, Red No. 3, Red No. 4, or Red
No. 40, water soluble D&C dyes, such as Yellow No. 10, Red
25 No. 22 or Red No. 28, and pyrogallol. Numerous other hair
dyes are listed in the *CTFA Handbook*, pages 70-71,
incorporated herein by reference.

The first topically active compound may also be an
30 antioxidant, such as ascorbic acid or erythorbic acid; or a
fluorescent whitening agent or optical brightener, such as a

- 23 -

distyrylbiphenyl derivative, stilbene or a stilbene derivative, a pyralozine derivative or a coumarin derivative. In addition, a self-tanning compound, such as dihydroxy acetone, or a hair growth promoter, or a hair
5 bleaching agent, such as perborate or a persulfate salt, can be the first topically active compound.

The first topically active compound can also be a deodorant compound, such as an astringent salt or a bioactive
10 compound. The astringent salts include organic and inorganic salts of aluminum, zirconium, zinc, and mixtures thereof. The anion of the astringent salt can be, for example, sulfate, chloride, chlorohydroxide, alum, formate, lactate, benzyl sulfonate or phenyl sulfonate. Exemplary
15 classes of antiperspirant astringent salts include aluminum halides, aluminum hydroxyhalides, zirconyl oxyhalides, zirconyl hydroxyhalides, and mixtures thereof.

Exemplary aluminum salts include aluminum chloride and the
20 aluminum hydroxyhalides having the general formula $Al_2(OH)_xQ_yXH_2O$; wherein Q is chlorine, bromine or iodine; x is about 2 to about 5; x+y is about 6, wherein x and y are not necessarily integers; and X is about 1 to about 6. Exemplary zirconium compounds include zirconium oxy salts
25 and zirconium hydroxy salts, also referred to as zirconyl salts and zirconyl hydroxy salts, and represented by the general empirical formula $ZrO(OH)_{2-nz}L_z$, wherein z varies from about 0.9 to about 2 and is not necessarily an integer; n is the valence of L; 2-nz is greater than or equal to 0;

- 24 -

and L is selected from halides, nitrate, sulfamate, sulfate, and mixtures thereof.

Exemplary deodorant compounds therefore include, but are not limited to, aluminum bromohydrate, potassium alum, sodium aluminum chlorohydrate, aluminum sulfate, aluminum chlorohydrate, aluminum-zirconium tetrachlorohydrate, an aluminum-zirconium polychlorohydrate complexed with glycine, aluminum-zirconium trichlorohydrate, aluminum-zirconium octachlorohydrate, aluminum sesquichlorohydrate, aluminum sesquichlorohydrate PG, aluminum chlorohydrate PEG, aluminum zirconium octachlorohydrate glycine complex, aluminum zirconium pentachlorohydrate glycine complex, aluminum zirconium tetrachlorohydrate glycine complex, aluminum zirconium trichlorohydrate glycine complex, aluminum chlorohydrate PG, zirconium chlorohydrate, aluminum dichlorohydrate, aluminum dichlorohydrate PEG, aluminum dichlorohydrate PG, aluminum sesquichlorohydrate PG, aluminum chloride, aluminum zirconium pentachlorohydrate, numerous other useful antiperspirant compounds listed in the CTFA Handbook at p. 56, (incorporated herein by reference), and mixtures thereof.

In addition to the astringent salts, the deodorant compound can be a bacteriostatic quaternary ammonium compound, such as, for example, cetyl trimethyl ammonium bromide, cetyl pyridinium chloride, benzethonium chloride, diisobutylbenzoxoethoxyethyl-dimethylbenzyl ammonium chloride, sodium N-lauryl sarcosine, sodium N-polymethyl sarcosine, lauroyl sarcosine, N-myristoyl glycine, potassium N-lauroyl sarcosine, and stearyl trimethyl

- 25 -

ammonium chloride; or a bioactive compound; or a carbonate or bicarbonate salt, such as, for example, the alkali metal carbonates and bicarbonates, and the ammonium and tetraalkylammonium carbonates and bicarbonates.

5

In addition, other compounds can be included in the primary emulsion as the first topically active compound in an amount sufficient to perform their intended function. For example, if the composition is intended to be a sunscreen, compounds
10 such as benzophenone-4, trihydroxycinnamic acid and salts, tannic acid, uric acid, quinine salts dihydroxy naphtholic acid; an anthranilate, diethanolamine methoxycinnamate, p-aminobenzoic acid, phenylbenzimidazole sulfonic acid, PEG-25 p-aminobenzoic acid or triethanolamine salicylate may be
15 incorporated into the internal aqueous W_1 phase.

Further, sunscreen compounds such as dioxybenzone, ethyl 4-[bis(hydroxypropyl)] aminobenzoate, glyceryl aminobenzoate, homosalate, menthyl anthranilate, octocrylene, octyl
20 methoxycinnamate, octyl salicylate, oxybenzone, padimate O, red petrolatum, titanium dioxide, 4-menthylbenzylidene camphor, benzophenone-1, benzophenone-2, benzophenone-7, benzophenone-12, isopropyl dibenzoyl methane, butyl methoxydibenzoylmethane, zotocrylene, or zinc oxide can be
25 incorporated into the oil phase of the primary emulsion. Other sunscreen compounds soluble in either the aqueous or organic phase are listed in *CTFA Handbook*, pages 87 and 87, (incorporated herein by reference).

30 Similarly, topically active drugs, such as antifungal compounds, antibacterial compounds; anti-inflammatory

- 26 -

compounds; topical anaesthetics; skin rash, skin disease and dermatitis medications; and anti-itch and irritation reducing compounds may be included in the compositions of the present invention. For example, analgesics such as
5 benzocaine, dyclonine hydrochloride, aloe vera and the like; anaesthetics such as butamben picrate, lidocaine hydrochloride, xylocaine and the like; antibacterials and antiseptics, such as povidone-iodine, polymyxin sulfate-bacitracin, zinc-neomycin sulfate-hydrocortisone,
10 chloramphenicol, methylbenzethonium chloride, and erythromycin and the like; antiparasitics, such as lindane; deodorants, such as chlorophyllin copper complex, aluminum chloride, aluminum chloride hexahydrate, and methylbenzethonium chloride; essentially all
15 dermatologicals, such as acne preparations, such as benzoyl peroxide, erythromycinbenzoyl peroxide, clindamycin phosphate, 5,7-dichloro-8-hydroxyquinoline, and the like; anti-inflammatory agents, such as alcometasone dipropionate, betamethasone valerate, and the like; burn relief ointments,
20 such as o-amine-p-toluene sulfonamide monoacetate and the like; depigmenting agents, such as monobenzone; dermatitis relief agents, such as the active steroid acinonide, diflorasone diacetate, hydrocortisone, and the like; diaper rash relief agents, such as methylbenzethonium chloride and
25 the like; emollients and moisturizers, such as mineral oil, PEG-4 dilaurate, lanolin oil, petrolatum, mineral wax and the like; fungicides, such as butocouazole nitrate, haloprogen, clotrimazole, and the like; herpes treatment drugs, such as O-[(2-hydroxyethoxy)-methyl]guanine; pruritic
30 medications, such as alcometasone dipropionate, betamethasone valerate, isopropyl myristate MSD, and the

- 27 -

like; psoriasis, seborrhea and scabicide agents, such as anthralin, methoxsalen, coal tar and the like; steroids, such as 2-(acetyloxy)-9-fluoro-1',2',3',4'-tetrahydro-11-hydroxypregna-1,4-dieno[16,17-b]naphthalene-3,20-dione and
5 21-chloro-9-fluoro-1',2',3',4'-tetrahydro-11b-hydroxypregna-1,4-dienol[16z,17-b]naphthalene-3,20-dione. Any other medication capable of topical administration also can be incorporated in a composition of the present invention in an amount sufficient to perform its intended function. Other
10 topically active compounds are listed in *Remington's Pharmaceutical Sciences*, 17th Ed., Merck Publishing Co, Easton, Pa. (1985), pages 773-791 and pages 1054-1048 (hereinafter *Remington's*), incorporated herein by reference.

15 An above-described first topically active compound is designed to remain on the skin or hair to perform its intended function. However, in particular situations, a first topically active compound that is rinsed from the skin or hair can be incorporated into the internal aqueous W_1
20 phase of the primary emulsion.

For example, a W_1 -O- W_2 multiple emulsion composition designed as a permanent wave composition can incorporate a reducing agent into the external aqueous phase as the second
25 topically active compound. After applying the W_1 -O- W_2 composition to the hair and allowing the composition to contact the hair for a sufficient time to reduce the hair, the external aqueous phase is rinsed from the hair leaving droplets of the primary emulsion on the hair.

30

- 28 -

The primary emulsion has incorporated therein an oxidizing agent as the first topically active compound. After the oil phase, and preferably a volatile oil phase, evaporates from the primary emulsion, the oxidizing agent is released to
5 neutralize the hair and any reducing agent remaining on the hair. Excess oxidizing agent can then be rinsed from the hair in a second rinsing step.

Exemplary, but non-limiting, oxidizing agents used as the
10 first topically active compound are ammonium persulfate, hydrogen peroxide, potassium bromate, potassium chromate, potassium persulfate, sodium bromate, sodium carbonate, peroxide, sodium iodate, sodium perborate, sodium persulfate, urea peroxide, and mixtures thereof. An
15 oxidizing agent may also be the second topically active compound when the first topically active compound is a hair conditioner. In addition, the second topically active compound may be a bleaching agent (i.e., an oxidizing agent) and the first topically active compound may be a hair dye.

20

In preferred embodiments of the invention, the topically active compound should not be cationic in nature, particularly if anionic surfactants are used.

25 Water

Sufficient water is present in the aqueous phase such that the aqueous phase comprises about 1% to about 99% by weight of the W_1O . Total water present in the W_1-O-W_2 multiple
30 emulsion composition is about 30% to about 99.9%, and

- 29 -

typically about 40% to about 95%, by weight of the composition.

Solutes

5

The internal aqueous phase must also include oil-insoluble solute(s). The solutes are introduced to balance osmotic pressure. Among solutes which may be added are organic or inorganic salts such as alkali metal chlorides, sulfates, 10 nitrates, benzoates and acetates and sugars and sugar derivatives, for example glucose and sucrose. Solute, when added to the internal aqueous phase, comprises 0.01 to 30% by wt., preferably 0.1 to 20%, most preferably 0.5 to 15%.

15 Optional Components

It is also possible to add surfactant to the internal aqueous phase though this is generally added to the external W₂ phase. The surfactant may be any of the surfactants 20 discussed in connection with the W₂ phase below.

The internal aqueous phase can also include optional ingredients traditionally included in topically applied compositions. These optional ingredients include, but are 25 not limited to, dyes, fragrances, preservatives, antioxidants, detackifying agents, and similar types of compounds. The optional ingredients are included in the internal aqueous phase of the primary emulsion in an amount sufficient to perform their intended function.

30

- 30 -

O Phase

The primary W_1/O emulsion also comprises about 0.5% to about 99%, preferably about 0.75% to about 80%, and most preferably about 1% to about 70%, by weight of the emulsion of an oil phase. The oil phase is comprised of an oil and a low HLB surfactant. The oil phase encapsulates the internal aqueous W_1 phase of the primary emulsion to form droplets of about 0.1 to about 1,000 μ , preferably about 1 to about 500 μ , in diameter. The oil phase therefore provides a barrier between the internal aqueous phase of the primary emulsion and the external aqueous phase of the W_1-O-W_2 multiple emulsion composition. The oil phase provides a sufficient barrier even though the oil phase constitutes as little as 0.5% by weight of the W_1O emulsion.

Oil

The oil may be volatile (except for silicone) or nonvolatile.

A volatile oil may comprise a volatile hydrocarbon oil which evaporates during the process of drying skin or hair, and thereby releases the internal aqueous W_1 phase, which includes the first topically active compound to contact the skin or hair. This oil preferably should contain no volatile silicone since volatile silicones tend to destabilize the multiple emulsion.

- 31 -

In one embodiment, the oil may comprise a combination of a volatile oil (except for silicone) and a nonvolatile oil. In this embodiment, an oil can be designed to evaporate at a pre-selected temperature and provide a controlled release of the first topically active compound at the pre-selected temperature. Pre-selected temperatures are those encountered during normal hair drying, provided by a hair dryer, or provided by a curling iron.

As previously stated, the oil may also include a water insoluble topically active compound in a sufficient amount to impart a particular functional or aesthetic effect (e.g., emolliency), as long as the topically active compound does not adversely affect the W_1 -O- W_2 multiple emulsion composition (e.g., does not impart emulsion instability).

Although the oil can incorporate a topically active compound, the topically active compound preferably is incorporated into the internal aqueous phase.

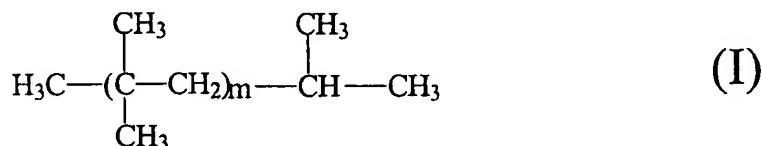
20

The volatile oil preferably comprises a volatile hydrocarbon compound, such as a hydrocarbon having about 10 to about 30 carbon atoms, that has sufficient volatility to slowly volatilize from the skin or hair after application of the W_1 -O- W_2 multiple emulsion composition to the skin or hair and subsequent rinsing. A preferred volatile hydrocarbon compound is an aliphatic hydrocarbon having about 12 to about 24 carbon atoms, and having a boiling point of about 100°C to about 250°C. The volatile hydrocarbon compounds

- 32 -

perform the same function and provide essentially the same benefits as the volatile silicone compounds.

Volatile hydrocarbon compounds incorporated into the primary emulsion include, for example, isododecane and isohexadecane, i.e., PERMETHYL 99A, PERMETHYL 101A and PERMETHYL 102A, available from Presperse, Inc., South Plainfield, N.J. Other exemplary volatile hydrocarbon compounds are depicted in general structural formula (I), wherein m ranges from 2 to 5.



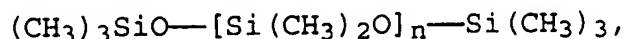
Another exemplary volatile hydrocarbon compound is ISOPAR M (a C₁₃-C₁₄ isoparaffin available from Exxon Chemical Co., Baytown, Tex). Preferably, the volatile hydrocarbon is less than 50% unsaturated.

As previously stated, the oil may also be a nonvolatile oil. The nonvolatile oil comprises a nonvolatile silicone compound, a nonvolatile hydrocarbon, or mixtures thereof. Preferably, the nonvolatile oil comprises compounds which contain less than 50% unsaturation. The nonvolatile oil phase does not evaporate from the skin or hair. The first topically active compound therefore is released by rubbing the skin or hair to rupture the W₁/O emulsion. A nonvolatile oil has a boiling point at atmospheric pressure of greater than about 250°C.

- 33 -

Exemplary nonvolatile silicone compounds include a polyalkyl siloxane, a polyaryl siloxane or a polyalkylaryl siloxane. Mixtures of these nonvolatile silicone compounds are also useful. The nonvolatile silicones are nonfunctional
5 siloxanes or siloxane mixtures having a viscosity of about 10 to about 600,000 cs, and typically about 350 to about 10,000 cs, at 25°C. The so-called "rigid silicones", as described in U.S. Patent No. 4,902,499, (herein incorporated by reference), having a viscosity above 600,000 cs at 20°C.,
10 and a weight average molecular weight of at least about 500,000, are also useful in compositions of the present invention. A phenyltrimethicone is also useful as a nonvolatile silicone compound.

15 Preferably the nonvolatile silicone compound is a nonvolatile polydimethylsiloxane compound, such as a mixture, in about a 2:1 weight ratio, of a low molecular weight polydimethylsiloxane fluid and a higher molecular weight polydimethylsiloxane gum. Preferred silicone gums
20 include linear and branched polydimethylsiloxanes of the general formula:



25 wherein n is a number from about 2,000 to about 15,000, and preferably from about 2,000 to about 7,000. Silicone gums useful in compositions of the present invention are available from a variety of commercial sources, including General Electric Company, Waterford, N.Y. and Dow Corning
30 Corp., Midland, Michigan.

- 34 -

The nonvolatile oil may also comprise a nonvolatile hydrocarbon compound, such as mineral oil. Other exemplary nonvolatile hydrocarbon compounds that may be used include, but are not limited to, a branched 1-decene oligomer, such as 1-decene dimer or a polydecene.

The oil may also further optionally comprise (1) an oil, such as jojoba oil, wheat germ oil or purcellin oil; or (2) a water insoluble emollient, such as, for example, an ester having at least about 10 carbon atoms, preferably about 10 to about 32 carbon atoms.

Suitable esters include those comprising an aliphatic alcohol having about eight to about twenty carbon atoms and an aliphatic or aromatic carboxylic acid including from two to about twelve carbon atoms, or conversely, an aliphatic alcohol having two to about twelve carbon atoms with an aliphatic or aromatic carboxylic acid including about eight to about twenty carbon atoms. The ester is either straight chained or branched. Preferably, the ester has a molecular wt. of less than about 500. Suitable esters therefore include, for example, but are not limited to:

- (a) aliphatic monohydric alcohol esters, for example:
- myristyl propionate,
 - isopropyl isostearate,
 - isopropyl myristate,
 - isopropyl palmitate,
 - cetyl acetate,
 - cetyl propionate,
 - cetyl stearate,

- 35 -

isodecyl neopentanoate,
cetyl octanoate,
isocetyl stearate;

- 5 (b) aliphatic di- and tri-esters of polycarboxylic acids,
for example:

diisopropyl adipate,
diisostearyl fumarate,
dioctyl adipate, and
10 triisostearyl citrate;

- (c) aliphatic polyhydric alcohol esters, for example:
propylene glycol dipelargonate;

- 15 (d) aliphatic esters of aromatic acids, for example:
C₁₂-C₁₅ alcohol esters of benzoic acid,
octyl salicylate,
sucrose benzoate, and
dioctyl phthalate.

20

Numerous other esters are listed in the *CTFA Handbook* at
pages 24 through 26, (incorporated herein by reference).

Low HLB Emulsifier

25

The O phase of the present invention also includes about
0.1% to about 30%, and preferably about 1% to about 15% of
the weight of the oil of a low HLB emulsifier.

- 30 The low HLB emulsifier may comprise a silicon-free
surfactant, or a blend of silicon-free surfactants, having

- 36 -

an HLB value of about less than 10 (i.e., an HLB value of about 0.1 to about less than 10), an oil-soluble silicon-based surfactant, an oil-soluble polymeric surfactant, or mixtures thereof. Preferably, the silicon-free surfactant or surfactant blend has an HLB value of about 1 to about 7,
5 more preferably about 3 to about 6. The term oil-soluble as used herein means a compound having a solubility of at least 0.1 g per 100 ml of oil phase to form a true solution.

10 The HLB value of a particular surfactant can be found in *McCutcheon's Emulsifiers and Detergents*, North American and International Editions, MC Publishing, Glen Rock, NJ (1993) (hereinafter *McCutcheon's*). Alternatively, the HLB value of a particular surfactant can be estimated by dividing the
15 weight percent of oxyethylene in the surfactant by five (for surfactants including only ethoxy moieties). In addition, the HLB value of a surfactant blend can be estimated by the following formula:

$$20 \quad \text{HLB} = (\text{wt.}\% \text{ A}) (\text{HLB}_A) + (\text{wt.}\% \text{ B}) (\text{HLB}_B),$$

wherein wt. % A and wt. % B are the weight percent of surfactants A and B in the silicon-free surfactant blend, and HLB_A and HLB_B are the HLB values for surfactants A and
25 B, respectively.

Suitable Low HLB surfactants may be a silicone-based surfactant or a silicone free surfactant.

- 37 -

Suitable classes of silicon-free nonionic surfactants include, but are not limited to, polyoxyethylene ethers of fatty (C₆-C₂₂) alcohols, polyoxyethylene/polyoxypropylene ethers of fatty (C₆-C₂₂) alcohols, ethoxylated alkylphenols, polyethylene glycol ethers of methyl glucose, polyethylene glycol ethers of sorbitol, and mixtures thereof.

Suitable silicon-free nonionic surfactants are the ethoxylated alcohols having an HLB value of about 0.1 to about 10. An especially preferred ethoxylated alcohol is laureth-1, i.e., lauryl alcohol ethoxylated with an average of one mole of ethylene oxide. Other suitable ethoxylated alcohols include laureth-2, laureth-3 and laureth-4. Numerous other suitable nonionic surfactants having an HLB of about 0.1 to about 10 are listed in McCutcheon s at pages 229-236, (incorporated herein by reference). Other exemplary silicon-free nonionic surfactants having an HLB value of about 0.1 to about 10 include, but are not limited to, the ethoxylated nonylphenols, ethoxylated octylphenols, ethoxylated dodecylphenols, ethoxylated fatty (C₆-C₂₂) alcohols having four or fewer ethylene oxide moieties, oleth-2, steareth-3, steareth-2, ceteth-2, oleth-3, and mixtures thereof.

The emulsifier may also comprise a silicon-free surfactant blend having an HLB value of about 1 to about 10. The blend is a mixture of a sufficient amount of a surfactant having an allowable HLB value, i.e., about 0.1 to about 10, and a sufficient amount of a surfactant having a higher HLB value, i.e., about 1 to greater than about 10, such that the

- 38 -

surfactant blend has an overall HLB value of about 1 to about 10. Exemplary, but non-limiting, nonionic surfactants having a high HLB value are listed in McCutcheon's at pages 236-246, (incorporated herein by reference).

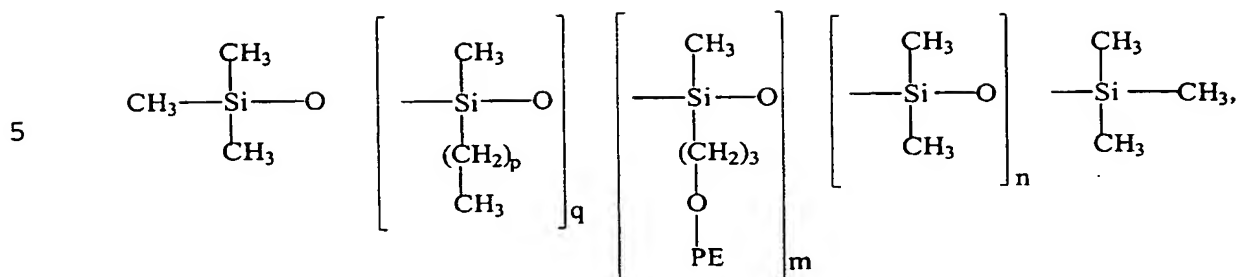
5

A preferred silicone free surfactant is PEG 30 dipolyhydroxystearate.

10 An exemplary oil-soluble silicon-based surfactant is a dimethicone copolyol, which is a dimethylsiloxane polymer having polyoxyethylene and/or polyoxypropylene side chains, such as DOW CORNING 3225C and 5225C FORMULATION AID, available from Dow Corning Co., Midland, Mich. The dimethicone copolyol has about 15 or fewer ethylene oxide
15 and/or propylene oxide monomer units, in total, in the side chains. Dimethicone copolyols are conventionally used in conjunction with silicones because the silicon-containing surfactants are extremely soluble in a volatile or a nonvolatile silicone compound, are extremely insoluble in
20 water, and have a low skin irritancy potential.

Another exemplary, but non-limiting, oil-soluble, silicon-based surfactant is an alkyl dimethicone copolyol, such as cetyl dimethicone copolyol available commercially as ABIL^(R)
25 EM 90 from Goldschmidt Chemical Corporation, Hopewell, Va. The alkyl dimethicone copolyols have the structure:

- 39 -



wherein:

- 10 p is a numeral from 7 to 17;
 q is a numeral from 1 to 100;
 m is a numeral from 1 to 40;
 n is a numeral from 0 to 200; and

- 15 PE is $(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b\text{-H}$ having a molecular weight of about 250 to about 2000, wherein a and b are selected such that the weight ratio of $\text{C}_2\text{H}_4\text{O}/\text{C}_3\text{H}_6\text{O}$ is from 100/0 to 20/80.

The surfactant phase may also comprise an oil-soluble
 20 polymeric surfactant. Polymeric surfactants capable of forming water-in-oil emulsions have the advantages that they completely cover the surface of the water droplet, are firmly anchored at the oil-water interface, the external oil phase is a good solvent for the stabilizing portion of the
 25 polymeric surfactant, and the thickness of the polymer layer on the oil side of the interface is sufficient to ensure stability. These surfactants may include ethoxy, propoxy and/or similar alkylene oxide monomer units, e.g., butoxy. The oil-soluble polymeric surfactants act as surfactants and
 30 are not physically or chemically cross-linked in solution.

- 40 -

The oil-soluble polymeric surfactants are therefore differentiated from polymeric gelling agents such as polyacrylic acid or polymethacrylic acid.

5 Accordingly, exemplary oil-soluble polymeric surfactants include, but are not limited to, polyoxyethylene-polyoxypropylene block copolymers, and similar polyoxyalkylene block copolymers. The oil-soluble block
10 copolymers typically have less than about 20% by weight of ethylene oxide. Specific non-limiting oil-soluble polymeric surfactants include Poloxamer 101, Poloxamer 105, PPG-2-Buteth-3, PPG-3-Butech-5, PPG-5-Butech-7, PPG-7-Butech-10, PPG-9-Buteth-12, PPG-12-Buteth-16, PPG-15-Buteth-20, PPG-20-Buteth-30, PPG-24-Buteth-27, PPG-28-Buteth-35, and PEG-15
15 Butanediol. Other useful oil-soluble polymeric surfactants are polyamines, i.e., polyoxyethylene-polyoxypropylene block copolymers of ethylene diamine, having less than about 40% by weight ethylene oxide.

20 The hydrophobic moiety of a silicon-free surfactant, silicon-containing surfactant or a polymeric surfactant is sufficiently soluble in the oil phase such that a sufficient amount of the surfactant is present in the oil phase to stabilize the primary W_1/O emulsion. In one embodiment when
25 the oil phase comprises a silicone compound, the surfactant phase comprises either a silicon-based surfactant, a silicon-free surfactant having a hydrophobic moiety preferably containing about ten to about fourteen carbon atoms, an oil-soluble polymeric surfactant, or a mixture
30 thereof. If the hydrophobic moiety of the silicon-free surfactant is saturated and includes more than about 14

- 41 -

carbon atoms, the silicon-free surfactant is insoluble in the silicone phase and the primary W_1/O emulsion is unstable. If the hydrophobic moiety includes less than about 10 carbon atoms, the primary W_1/O emulsion has a
5 tendency to coalesce i.e., the emulsion droplets fuse to form large droplets. The amount of surfactant phase necessary to provide a primary emulsion of desired W_1/O droplet diameter varies with the amount of aqueous phase in the primary emulsion and is easily determined by those
10 skilled in the art.

A particularly preferred emulsifier is cetyl dimethicone copolyol.

15 The External Aqueous Phase

In the first embodiment, the external aqueous phase (W_2) of the W_1-O-W_2 multiple emulsion comprises an isotropic mixture of surfactants phase (as opposed to lamellar phase of U.S.
20 Patent No. 5,656,280). As noted, this external phase comprises a non-amido anionic surfactant and/or other surfactant. Preferably, it comprises anionic in combination with amphoteric surfactants wherein the nonamido group anionic comprises 1 to 99% of the surfactant system and
25 amphoteric comprises 1 to 99% of the surfactant system. The key to the invention is that much greater levels of surfactants may be used than previously believed possible while maintaining a stable multiple emulsion.

- 42 -

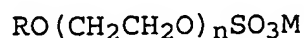
In the second embodiment the external aqueous phase (W_2) of the W_1 -O- W_2 multiple emulsion comprises a relatively high level of surfactant(s) that form an isotropic phase, a second topically effective compound, typically 0-40% by wt. of the external phase to perform a function identical to, similar to or different from the first topically active compound, solute, and 0.01 to 10% by wt. of a stabilizing natural gum polymer. The composition contains all non-amido anionic or all amphoteric surfactant, or combinations of the two. The surfactant typically comprises about 2-80% of the aqueous phase.

The anionic surfactant in either of the above embodiment may be, for example, an aliphatic sulfonate, such as a primary alkane (e.g., C_8 - C_{22}) sulfonate, primary alkane (e.g., C_8 - C_{22}) disulfonate, C_8 - C_{22} alkene sulfonate, C_8 - C_{22} hydroxyalkane sulfonate or alkyl glyceryl ether sulfonate (AGS); or an aromatic sulfonate such as alkyl benzene sulfonate.

20

The anionic may also be an alkyl sulfate (e.g., C_{12} - C_{18} alkyl sulfate) or alkyl ether sulfate (including alkyl glyceryl ether sulfates). Among suitable alkyl ether sulfates are those having the general formula:

25



wherein R is an alkyl or alkenyl group having about 8 to 18 carbons, preferably 12 to 18 carbons, n has an average value

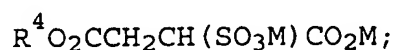
- 43 -

of greater than 1.0, preferably between 2 and 3; and M is a solubilizing cation such as sodium, potassium, ammonium or substituted ammonium. Ammonium and sodium lauryl ether sulfates are preferred.

5

The anionic may also be alkyl sulfosuccinates (including mono- and dialkyl, e.g., C₆-C₂₂ sulfosuccinates); alkyl and acyl taurates, alkyl and acyl sarcosinates, sulfoacetates, C₈-C₂₂ alkyl phosphates and phosphates, alkyl phosphate
10 esters and alkoxyl alkyl phosphate esters, acyl lactates, C₈-C₂₂ monoalkyl succinates and maleates, sulphoacetates, and acyl isethionates.

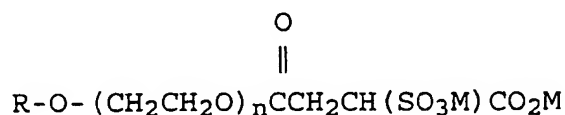
Sulfosuccinates may be monoalkyl sulfosuccinates having the
15 formula:



wherein R⁴ ranges from C₈-C₂₂ alkyl and M is a solubilizing
20 cation defined above;

Also included are the alkoxylated citrate sulfosuccinates; and alkoxylated sulfosuccinates such as the following:

25



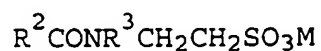
wherein n = 1 to 20; and M is as defined above.

30

- 44 -

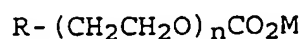
Sarcosinates are generally indicated by the formula $RCON(CH_3)CH_2CO_2M$, wherein R ranges from C_8 to C_{20} alkyl and M is a solubilizing cation.

5 Taurates are generally identified by the formula



wherein R^2 ranges from C_8 - C_{20} alkyl, R^3 ranges from C_1 - C_4
10 alkyl and M is a solubilizing cation.

Another class of anionics are carboxylates such as follows:



15

wherein R is C_8 to C_{20} alkyl; n is 0 to 20; and M is as defined above.

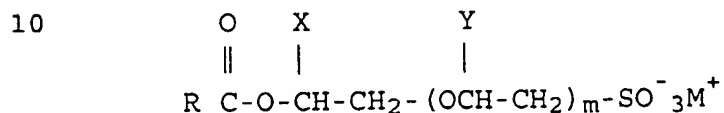
Another carboxylate which can be used is amido alkyl
20 polypeptide carboxylates such as, for example, Monteine LCQ^(R) by Seppic.

Other surfactants which may be used are the C_8 - C_{18} acyl isethionates. These esters are prepared by reaction between
25 alkali metal isethionate with mixed aliphatic fatty acids having from 6 to 18 carbon atoms and an iodine value of less than 20. At least 75% of the mixed fatty acids have from 12 to 18 carbon atoms and up to 25% have from 6 to 10 carbon atoms.

- 45 -

Acyl isethionates, when present, will generally range from about 0.5-15% by weight of the total composition, preferably, from about 1 to about 10%.

5 The acyl isethionate may be an alkoxyated isethionate such as is described in Ilardi et al., U.S. Patent No. 5,393,466, (hereby incorporated by reference). This compound has the general formula:



wherein R is an alkyl group having 8 to 18 carbons, m is an
 15 integer from 1 to 4, X and Y are hydrogen or an alkyl group having 1 to 4 carbons and M^+ is a monovalent cation such as, for example, sodium, potassium or ammonium.

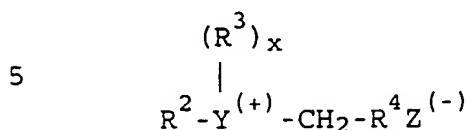
In general the anionic component will comprise from about 1
 20 to 30% by weight of the composition, preferably 2 to 25%, most preferably 5 to 20% by weight of the composition.

Zwitterionic and Amphoteric Surfactants

25 Zwitterionic surfactants are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals may be straight or branched chain, and wherein one of the aliphatic substituents contains from
 30 about 8 to about 18 carbon atoms and one contains an anionic

- 46 -

group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical containing about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

4- [N,N-di (2-hydroxyethyl) -N-octadecylammonio] -butane-1-carboxylate;

5- [S-3-hydroxypropyl-S-hexadecylsulfonio] -3-hydroxypentane-1-sulfate;

3- [P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio] -2-hydroxypropane-1-phosphate;

3- [N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio] -propane-1-phosphonate;

3- (N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;

- 47 -

3 - (N,N-dimethyl-N-hexadecylammonio) - 2-hydroxypropane-1-sulfonate;

4 - [N,N-di (2-hydroxyethyl) -N- (2-hydroxydodecyl) ammonio] - butane-1-carboxylate;

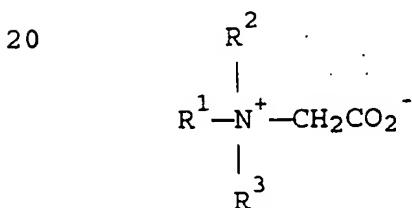
5 3 - [S-ethyl-S- (3-dodecoxy-2-hydroxypropyl) sulfonio] - propane-1-phosphate;

3 - [P,P-dimethyl-P-dodecylphosphonio] -propane-1-phosphonate; and

10 5 - [N,N-di (3-hydroxypropyl) -N-hexadecylammonio] -2-hydroxy-pentane-1-sulfate.

Amphoteric detergents which may be used in this invention include at least one acid group. This may be a carboxylic or a sulphonic acid group. They should generally include an
15 alkyl or alkenyl group containing 7 to 18 carbon atoms.

Suitable amphoteric detergents within the above general formula include simple betaines of formula:



where R^1 is alkyl or alkenyl of 7 to 18 carbons; R^2 and R^3 are each independently alkyl, hydroxyalkyl or carboxyalkyl containing 2 to 3 carbon atoms.

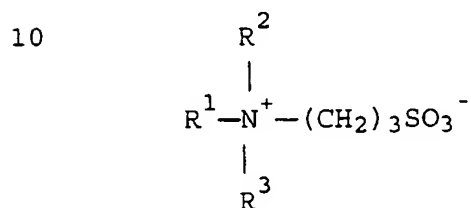
30

R^1 may in particular be a mixture of C_{12} and C_{14} alkyl groups derived from coconut so that at least half, preferably at

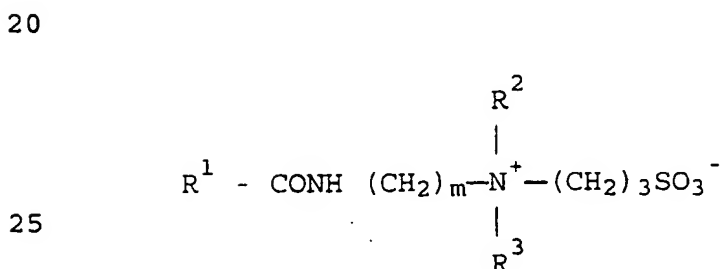
- 48 -

least three quarters of the groups R^1 have 10 to 14 carbon atoms. R^2 and R^3 are preferably methyl.

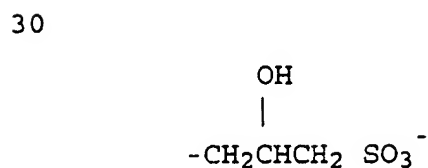
A further possibility is that the amphoteric detergent is a sulphobetaine of formula:



or



where m is 2 or 3, or variants of these in which $-(CH_2)_3 SO_3^-$ is replaced by



wherein R^1 , R^2 and R^3 are as defined previously.

- 49 -

The amphoteric/zwitterionic surfactant generally comprises about 1 to 30% by weight, preferably 2 to 25% of the composition, more preferably 5 to 20%.

- 5 In addition to one or more anionic and amphoteric and/or zwitterionic, the surfactant system may optionally comprise a nonionic surfactant.

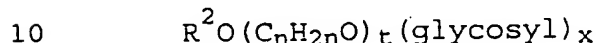
The nonionic which may be used includes in particular the
10 reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are
15 alkyl (C₆-C₂₂) phenols-ethylene oxide condensates, the condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, and products produced by condensation of ethylene oxide with the reaction products of propylene oxide and
20 ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

The nonionic may also be a sugar amide, such as a
25 polysaccharide amide. Specifically, the surfactant may be one of the lactobionamides described in U.S. Patent No. 5,389,279 to Au et al. which is hereby incorporated by reference or it may be one of the sugar amides described in Patent No. 5,009,814 to Kelkenberg, hereby incorporated into
30 the subject application by reference.

- 50 -

Other surfactants which may be used are described in U.S. Patent No. 3,723,325 to Parran Jr. and alkyl polysaccharide nonionic surfactants as disclosed in U.S. Patent No. 4,565,647 to Llenado, both of which are also incorporated
5 into the subject application by reference.

Preferred alkyl polysaccharides are alkylpolyglycosides of the formula:



wherein R^2 is selected from alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which alkyl groups contain from about 10 to about 18,
15 preferably from about 12 to about 14, carbon atoms; n is 0 to 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from 1.3 to about 10, preferably from 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy
20 alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units may then be attached between the 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly
25 the 2-position.

Nonionic comprises 0 to 10% by wt. of the composition.

According to a second embodiment, the external aqueous phase
30 must also comprise about 0.01 to 10% by wt of a

- 51 -

stabilizing natural gum polymer. It is preferred that in systems where the external surfactant W2 is comprised entirely of or contains a majority of (60% or higher) anionic surfactant that a nonionic gum polymer is used.

5

Nonionic seed polysaccharides are particularly soluble and dispersible in anionic surfactants and anionic rich surfactant systems. One such stabilizer is guar gum, which is structurally composed of a straight chain of D-mannose
10 with a D-galactose side chain on approximately every other mannose unit. The usual ratio of mannose to galactose is approximately 2:1 and molecular weights are usually on the order of 100,000 to 1,000,000. Another useful stabilizer is locust bean gum, a galactomannan consisting of a main chain
15 of D-mannose units with single galactose side chains on approximately every fourth unit. As with guar gum, approximate molecular weights are between 100,000 and 1,000,000.

20 In systems where the external surfactant W2 is comprised entirely of or contains a majority (50% or higher), of amphoteric surfactant, an anionic gum polymer is preferred. These may be seaweed polysaccharides, exudate polysaccharides, or microbial polysaccharides.

25

A preferred anionic seaweed polysaccharide is carrageenan, or Irish moss, a complex mixture of sulfated polysaccharides. Carrageenan is a mixture of galactans that carry varying proportions of half-ester sulfate groups
30 linked to one or more of the hydroxyl groups of the galactose units, which are joined by alternating α -1,3 and

- 52 -

β -1,4 glycosidic linkages. The molecular weight usually ranges from 100,000 to 1,000,000.

A preferred anionic exudate polysaccharide is gum
5 tragacanth, a complex mixture of acidic polysaccharides containing galacturonic acid, galactose, fucose, xylose, and arabinose. Another preferred anionic exudate polysaccharide is gum karaya, a partially acetylated high molecular weight polysaccharide which contains L-rhamnose, D-galactose, D-
10 galacturonic acid, and D-glucuronic acid residues.

The most preferred amphoteric or amphoteric rich surfactant systems are microbial anionic hetero polysaccharide gums, most preferably Xanthan gum. The primary structure of these
15 microbial gums contains two glucose units, two mannose units, and one glucuronic acid unit.

Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this
20 description indicating amounts or ratios of materials or conditions or reaction, physical properties of materials and/or use are to be understood as modified by the word "about".

25 Where used in the specification, the term "comprising" is intended to include the presence of stated features, integers, steps, components but not to preclude the presence or addition of one or more features, integers, steps, components or groups thereof.

30

- 53 -

All percentages used, unless indicated otherwise, are intended to be percentages by weight.

Definition and Measurement of Stability (for purposes of
5 first embodiment)

Sodium ISE: To measure multiple emulsion stability, a sodium ion sensitive electrode (Corning 476138) was attached to an Orion EA 920 expandable ion analyzer.

10

The multiple emulsion samples were intentionally prepared with a too low internal NaCl concentration. Thus, the Na ion concentration of the separated bottom phase served as a rapid indicator of multiple emulsion stability.

15

In the case of multiple emulsion breakage, the NaCl from the internal phase is released and the NaCl concentration in the external aqueous phase increases because the initial salt concentration is greater in the internal phase. A plot of
20 separated phase sodium ion concentration versus storage time shows a positive slope (increasing Na ion concentration over time).

In the case of a stable multiple emulsion, the NaCl is held
25 in the internal phase and only water is released to the external phase. A plot of separated phase sodium ion concentration versus storage time shows a negative slope (gradual Na ion dilution over time) or virtually no slope (water was released at an early stage).

30

- 54 -

5g of the separated external aqueous (bottom) phase was taken from the separatory funnel and diluted to 50 g with 45 g of milli-Q water. To this was added 50 g of 0.5 M triethanolamine (TEA) to maintain ionic strength and equalize activity coefficients.

Standards were prepared by taking 1,2, 3, 4 and 5 g samples of the original external phase and diluting them with 49, 48, 47, 46, and 45 g of milli-Q water, respectively, to 50 g. 50 g of 0.5 M TEA was added to each sample, as above.

Each of the standard samples and the separated emulsion sample were measured for sodium ion activity (concentration) using the sodium ion sensitive electrode.

15

Those multiple emulsions which showed a zero or negative slope over the course of 30 days at room temperature (20-25°C) storage were deemed stable. Conversely, those which displayed a positive slope over the same amount of time were deemed unstable.

Definition and Measurement of Stability (for second embodiment)

25 Multiple emulsion stability was measured after 45 days by collecting the amount of separated water phase (if any) and measuring the weight of collected material. This weight is then divided by the total weight of product in the separatory funnel to obtain % separation.

30

- 55 -

Multiple Emulsion Preparation (for both embodiments)Primary (W_1/O) Emulsions

5 Oil Phase: The oil and the oil soluble surfactant (low HLB emulsifier) were mixed together at room temperature using overhead stirring.

Internal aqueous phase (W_1): Sodium chloride solutions with
10 or without topically active compounds of appropriate concentrations were prepared and the pH was adjusted to 7.0.

W_1/O preparation: the oil phase (O) was charged into the vessel. The salt/topically active compound solution (W_1)
15 was added to the oil phase steadily through the addition funnel over the course of 10-12 minutes while mixing with the side scraper (60-80 rpm). Slow addition of aqueous phase under low shear mixing is essential to obtain a stable primary emulsion. Upon complete addition of the aqueous
20 phase, the mixing speed of the side scraper was reduced to 40 rpm and the homogenizer was turned on. Homogenization was carried out for 3 minutes each at 8000, 9500 and 13,500 rpm at room temperature. The heat generated during the homogenization process raised the temperature of the batch
25 to ~35°C.

Multiple Emulsion

External aqueous phase (W_2): External aqueous phases were
30 prepared in a jacketed vessel by mixing the minority

- 56 -

surfactant into the majority surfactant at 60°C with intense mixing. The pH of each surfactant solution was pre-adjusted to 7.0. Surfactant solutions which had a gel like consistency were centrifuged at 7000 rpm for 20 minutes to
5 remove the entrapped air.

W₁/O/W₂ preparation: The primary emulsion (W₁/O) was charged into the smaller scale vessel followed by addition of the external aqueous phase (W₂). The mixture was hand-
10 mixed gently for 15 seconds using a spatula. This was followed by mixing with the side-scraper for 8 minutes at 70-105 rpm (higher speed was used when mixing at lower speed was found to be inadequate). A small spatula was inserted
15 into the vessel as a baffle to ensure good mixing around the center spindle of the side scraper. The resulting multiple emulsions were transferred into 250 ml separatory funnels to await separation of the aqueous phase for emulsion stability analysis.

20 Examples 1-37 relate to the first embodiment and 38-59 relate to the second.

EXAMPLES

25 The following components were used in the experiment as follows;

- 57 -

Phase	Material	Supplier	Trade name	Function
	Milli-Q Water			
	Sodium Chloride	Fisher		Internal Solute
W1	Lactic Acid	Fluka		Benefit Agent
	Glucose	Aldrich		Benefit Agent
	Potassium Hydroxide	Fisher		
	Polyquaternium 11	ISP Corp.	GAFQUAT 755N	Hair Styling Polymer
	Poly(vinylpyrrolidone)	ISP Corp.	PVP K-120	Hair Styling Polymer
	Light Mineral (Paraffin) Oil	Fisher		Emollient
	Heavy Mineral (Paraffin) Oil	Fisher		Emollient
	Sunflower Oil	Clark/Welch		Emollient
	Octyl Palmitate	Goldschmidt	Tegosoft OP	Emollient
(O)il	Non volatile Silicone (Dimethicone) Oil	Dow Corning	DC 200 Fluid 50cst	Emollient
	Cetyl dimethicone copolyol	Goldschmidt	Abil EM 90	Low HLB surf.
	Cocoamidopropyl betaine	Goldschmidt	Tego Betain F 50	Amphoteric High HLB surf.
	Cocoamphoglycinate	McIntyre	Mackam 1C	" "
	Sodium laureth sulfate (SLES)	Stepan	Steol CS-330L	Anionic High HLB Surfactant
W2	Sodium lauryl sulfate (SDS)	Fluka		" "
	Sodium cocoyl isethionate	PPG Indust.	Jordapon CI	" "
	Alkanol carboxylate	Shell	Neodox 23-4	" "
	Lauryl ether sulfosuccinate	McIntyre	Mackanate EL	" "
	Disodium cocamido MEA sulfosuccinate	McIntyre	Mackanate CM	" "
	Disodium cocamido MIPA sulfosuccinate	McIntyre	Mackanate CP	" "
	Acylamine polyglycol ether sulfate	Hoechst AG	Genapol AMS	" "
	Decyl polyglucose	Henkel/Emery	Plantaren 2000	Nonionic High HLB Surfactant

- 58 -

EXAMPLES 1-14

In order to show the effect of varying anionics in mixture
with amphoterics (e.g., betaine) on multiple emulsion
5 stability, the following examples were prepared:

Table 1. Effect of different anionics in mixture with betaine on multiple emulsion stability

Formula #	1	2	3	4	5	6	7	8	9	10	11	12	13	14
W1 Phase														
Water	40.3	39.9	40.3	39.9	39.9	39.9	39.9	40.3	39.9	40.3	39.9	40.3	39.9	39.5
Sodium Chloride	1.7	2.1	1.7	2.1	2.1	2.1	2.1	1.7	2.1	1.7	2.1	1.7	2.1	2.5
(O)II Phase														
Light Paraffin Oil	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2
Cetyl dimethicone copolyol	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
W2 Phase														
Water	26.4	26.4	25	25	28.6	28.6	28.6	25	25	25	25	25	25	25
Cocamidopropyl betaine	8.2	8.2	9	9	6.8	6.8	6.8	9	9	9	9	9	9	9
Sodium laureth sulfate	5.4	5.4												
Sodium lauryl sulfate			6	6										
Sodium cocoyl isethionate					4.6									
Alkanol carboxylic acid						4.6								
Lauryl ether sulfosuccinate							4.6							
Disodium cocamido MEA sulfosuccinate								6	6					
Disodium cocamide MPA sulfosuccinate										6	6			
Acylaminopolyglycol ether sulfate												6	6	6
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stability of Multiple emulsion after 30 days at room temperature	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Unstable	Unstable	Unstable	Unstable	Unstable	Unstable	Unstable

As clearly seen, anionic surfactants with amido group render the multiple emulsion unstable (Examples 8 to 14 compared to 1 to 7).

- 60 -

EXAMPLES 15-21

In order to determine effect, if any, of amphoteric/anionic ratio on stability, the following examples were prepared:

5

Table 2. Effect of amphoteric/anionic ratio on multiple emulsion stability

Formula #		15	16	17	18	1	2	19	20	21
W1 Phase	Water	40.3	39.9	38.2	39.9	40.3	39.9	40.7	41.8	41.8
	Sodium Chloride	1.7	2.1	3.8	2.1	1.7	2.1	1.3	0.2	0.2
(O)il Phase	Light Paraffin Oil	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2
	Cetyl dimethicone copolyol	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
W2 Phase	Water	28.6	28.6	28.6	28.6	26.4	26.4	28.6	28.6	28.6
	Cocamidopropyl betaine	11.4	11.4	11.4	9.1	8.2	8.2	4.6	2.3	
	Sodium laureth sulfate				2.3	5.4	5.4	6.8	9.1	11.4
Total		100	100	100	100	100	100	100	100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Stable

10 As noted, regardless of amphoteric/anionic ratio, emulsion was stable.

EXAMPLES 1 and 22

15 From the following examples, it can be seen that multiple emulsion may be stable over various types of amphoterics.

- 61 -

Table 3. Effect of different amphotericics with anionic on multiple emulsion stability

5

Formula #		1	22
W1 Phase	Water	40.3	40.7
	Sodium Chloride	1.7	1.3
(O)il Phase	Light Paraffin Oil	16.2	16.2
	Cetyl dimethicone copolyol	1.8	1.8
W2 Phase	Water	26.4	28.6
	Cocamidopropyl betaine	8.2	
	Cocoamphoglycinate		6.8
	Sodium laureth sulfate	5.4	4.6
Total		100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable

EXAMPLES 23 and 24

- 10 The following compositions were prepared to show that nonionics and amphotericics also form stable multiple emulsions

- 62 -

Table 4. Effect of nonionics with amphoteric on multiple emulsion stability

Formula #		23	24
W1 Phase	Water	40.3	39.9
	Sodium Chloride	1.7	2.1
(O)il Phase	Light Paraffin Oil	16.2	16.2
	Cetyl dimethicone copolyol	1.8	1.8
W2 Phase	Water	25	25
	Cocamidopropyl betaine	9	9
	Decyl polyglucose	6	6
Total		100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable

5

EXAMPLES 1 AND 25-28

From the following table, it can be seen that stable multiple emulsions are formed when the composition of the oil phase is less than 50% unsaturated hydrocarbon compounds, i.e. sunflower oil has a composition which is greater than 50% unsaturated hydrocarbon compounds.

10

- 63 -

Table 5. Effect of different oils on multiple emulsion stability

Formula #		1	25	26	27	28
W1 Phase	Water	40.3	40.3	41.6	40.3	41.6
	Sodium Chloride	1.7	1.7	0.4	1.7	0.4
(O)il Phase	Light Paraffin Oil	16.2				
	Heavy Paraffin Oil		16.2			
	Octyl Palmitate			16.2		
	Non volatile Dimethicone Oil				16.2	
	Sunflower Oil					16.2
	Cetyl dimethicone copolyol	1.8	1.8	1.8	1.8	1.8
W2 Phase	Water	26.4	26.4	26.4	26.4	26.4
	Cocamidopropyl betaine	8.2	8.2	8.2	8.2	8.2
	Sodium laureth sulfate	5.4	5.4	5.4	5.4	5.4
Total		100	100	100	100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable	Stable	Stable	Unstable

5

EXAMPLES 29-31

10 In order to show the effect of low HLB emulsifier concentration, the following examples were prepared.

- 64 -

Table 6. Effect of emulsifier concentration on multiple emulsion stability

Formula #		29	30	31
W1 Phase	Water	38.2	38.2	38.2
	Sodium Chloride	3.8	3.8	3.8
(O)il Phase	Light Paraffin Oil	17.1	16.2	14.4
	Cetyl dimethicone copolyol	0.9	1.8	3.6
W2 Phase	Water	26.4	26.4	26.4
	Cocamidopropyl betaine	8.2	8.2	8.2
	Sodium laureth sulfate	5.4	5.4	5.4
Total		100	100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Un-stable	Stable	Stable

5

EXAMPLES 2, 32 AND 33

To show whether multiple emulsions are stable over broad composition of surfactant/oil ratios, the following examples
 10 were prepared:

- 65 -

Table 7. Effect of total surfactant/oil ratio on multiple emulsion stability

Formula #		2	32	33
W1 Phase	Water	39.9	20	6.7
	Sodium Chloride	2.1	1.1	0.4
(O)il Phase	Light Paraffin Oil	16.2	8.1	2.7
	Cetyl dimethicone copolyol	1.8	0.9	0.3
W2 Phase	Water	26.4	46.1	59.3
	Cocamidopropyl betaine	8.2	14.3	18.4
	Sodium laureth sulfate	5.4	9.5	12.2
Total		100	100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable	Stable

5

As clearly seen, the stability remained over a broad range of surfactant/oil ratios.

10

EXAMPLES 2, 34-37

In order to show the stability of the multiple emulsion when a skin benefit agent or hair styling polymer is incorporated into the W1 phase, Compositions 2 and 34-37 were prepared.

15

- 66 -

Table 8. Effect of incorporating benefit agent (lactic acid) into W1 phase on multiple emulsion stability

5

Formula #		2	34	35	36	37
W1 Phase	Water	39.9	36.5	36.9	24.5	26.6
	Sodium Chloride	2.1	2.1	2.1	0.7	0.7
	Lactic Acid		2.1			
	Potassium Hydroxide		1.3			
	Glucose			3		
	Polyquaternium 11				2.8	
	Poly(vinylpyrrolidone)					0.7
(O)il Phase	Light Paraffin Oil	16.2	16.2	16.2	10.8	10.8
	Cetyl dimethicone copolyol	1.8	1.8	1.8	1.2	1.2
W2 Phase	Water	26.4	24.5	24.4	42	42
	Cocamidopropyl betaine	8.2	7.4	8.2		
	Sodium laureth sulfate	5.4	4.9	5.4		
	Sodium lauryl sulfate				18	18
	Lactic Acid		2			
	Potassium Hydroxide		1.2			
	Glucose			2		
Total		100	100	100	100	100
Stability of	Multiple Emulsion after 30 days at room temperature	Stable	Stable	Stable	Unstable*	Stable*
* = determined by optical microscopy						

As clearly seen, in Examples 34 and 35, incorporation of benefit agent had no effect on multiple emulsion stability.

10 Examples 36 and 37 demonstrate the criticality that if a cationic hair styling polymer is used in systems containing

- 67 -

an anionic surfactant, multiple emulsion stability will be adversely affected.

Materials (for second embodiment) and Examples 38-59

5

The following components were used in the experiments as follows:

Phase	Material	Supplier	Trade name	Function
	Milli-Q Water			
W1	Sodium Chloride	Fisher		Internal Solute
	Glycerol	Dow		Benefit Agent
	Potassium Hydroxide	Fisher		
	Light Mineral (Paraffin) Oil	Fisher		Emollient
(O)il	Octyl Palmitate	Goldschmidt	Tegosoft OP	Emollient
	Cetyl dimethicone copolyol	Goldschmidt	Abil EM 90	Low HLB surf.
	Cocoamidopropyl betaine	Goldschmidt	Tego Betain F 50	Amphoteric High HLB surf.
	Cocoamphoglycinate	McIntyre	Mackam 1C	" "
W2	Sodium laureth sulfate (SLES)	Stepan	Sted CS-330L	Anionic High HLB Surfactant
	Sodium lauryl sulfate (SDS)	Fluka		" "
	Glycerol	Dow		Benefit Agent
	Locust Bean Gum	Fluka		Nonionic Natural Gum Stabilizer
	Guar Gum	Fluka		Nonionic Natural Gum Stabilizer
	Xanthan Gum	Fisher		Anionic Natural Gum Stabilizer
	Gum Tragacanth	Fluka		Anionic Natural Gum Stabilizer
	Gum Karaya	Fluka		Anionic Natural Gum Stabilizer
	Carrageenan	Fluka		Anionic Natural Gum Stabilizer

- 68 -

EXAMPLES 38-43

		Formula # 38	Formula # 39	Formula # 40	Formula # 41	Formula # 42	Formula # 43
	Water	39.8	39.8	39.8	39.8	39.8	
W1 Phase	Sodium Chloride	0.2	0.2	0.2	0.2	0.2	
	Glycerol	2	2	2	2	2	
Oil Phase	Light Paraffin Oil	16.2	16.2	16.2	16.2		
	Octyl Palmitate					16.2	
	Cetyl Dimethicone Copolyol	1.8	1.8	1.8	1.8	1.8	
	Water	23	22	21	22	22	66
	Sodium Laureth Sulfate	15	15	15		15	25
W2 Phase	Sodium Lauryl Sulfate				15		
	Glycerol	2	2	2	2	2	5
	Locust Bean Gum		1		1	1	
	Guar Gum			2			
	Xanthan Gum						4
Total		100	100	100	100	100	100
% Phase Sep. d45		40	0	15	N/A	0	
W2 Visc (cps) at 5 RPM		60	24,000	21,000	26,000	24,000	2 phase
W2 Visc (cps) at 50 RPM		60	7000	4500	8500	7500	

- 69 -

Example 38, the control, has a Newtonian anionic external W2 phase (SLES) and it phase separates 40% over 45 days. Examples 2 and 3 show that by gelling the external phase with a nonionic natural gum stabilizer, phase separation is prevented by incorporating locust bean gum or retarded by incorporating guar gum. Example 41 shows that Locust bean gum also gels another anionic surfactant, sodium lauryl sulfate. Example 42 shows that octyl palmitate can be substituted for light mineral oil. In Example 43, we attempted to incorporate an anionic gum into an anionic surfactant but the W2 phase was not homogeneous. Examples 39-42 show the criticality that the gum must be nonionic when the surfactant is anionic.

EXAMPLES 44-51

		Formula # 44	Formula # 45	Formula # 46	Formula # 47	Formula # 48	Formula # 49	Formula # 50	Formula # 51
	Water	34.8	34.8	34.8	34.8	34.8	34.8	34.8	
W1 Phase	Sodium Chloride	5.2	5.2	5.2	5.2	5.2	5.2	5.2	
	Glycerol	2	2	2	2	2	2	2	
Oil Phase	Light Paraffin Oil	16.2	16.2	16.2	16.2	16.2	16.2		
	Octyl Palmitate							16.2	
	Cetyl Dimethicone Copolyol	1.8	1.8	1.8	1.8	1.8	1.8	1.8	
	Water	23	22	21	21	20	22	22	66
	Cocoamido-propyl Betaine	15	15	15	15	15		15	25
W2 Phase	Cocaoamphoglycinate						15		5
	Glycerol	2	2	2	2	2	2	2	
	Xanthan Gum		1				1	1	
	Gum Karaya				2				
	Carrageenan					3			
	Locust Bean Gum								4
Total		100	100	100	100	100	100	100	100
% Phase Sep. d45									
W2 Visc (cps) at 20 RPM		50	0	5	10	10	N/A	0	
W2 Visc (cps) at 50 RPM		80	7,000	6,000	6,000	6,500	6,000	7,000	2 phase
		80	2,100	1,400	1,400	1,700	1,500	2,300	

- 71 -

Example 44, the control, has a Newtonian amphoteric external W2 phase (betaine) and it phase separates 50% over 45 days. Examples 45 through 49 show that by gelling the external phase with an anionic natural gum stabilizer, phase separation is prevented by incorporating xanthan gum or retarded by incorporating gum tragacanth, gum karaya, or carrageenan. Example 49 shows that xanthan gum also gels another amphoteric surfactant, cocoamphoglycinate. Example 50 shows that octyl palmitate can be substituted for light mineral oil. In Example 51, we attempted to incorporate a nonionic gum into an amphoteric surfactant but the W2 phase was not homogeneous. Examples 45-50 thus show that the gum must be anionic when the surfactant is amphoteric.

- 72 -

EXAMPLES 52-59

		Formula # 52	Formula # 53	Formula # 54	Formula # 55	Formula # 56	Formula # 57	Formula # 58	Formula # 59
	Water	39.6	39.6	39.6	39.6	36.4	36.4	36.4	36.4
	Sodium Chloride	0.4	0.4	0.4	0.4	3.6	3.6	3.6	3.6
	Glycerol	2	2	2	2	2	2	2	2
	Light Paraffin Oil	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2
	Cetyl Dimethicone Copolyol	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	Water	23	22	22	22	23	22	22	22
	Cocoamidopropyl Betaine	2	2	2	6	11	11	11	7.5
	Sodium Laureth Sulfate	13	13	13	9	4	4	4	7.5
	Glycerol	2	2	2	2	2	2	2	2
	Xanthan Gum		1					1	1
	Locust Bean Gum			1	1		1		
	Total	100	100	100	100	100	100	100	100
	% Phase Sep. d45	50	40	0	0	40	40	0	0
	W2 Visc (cps) at 5 RPM	100	200	27,000	30,000	4,000	4,500	8,000	28,000
	W2 Visc (cps) at 50 RPM	100	350	8,000	9,000	500	650	2,200	7,600

- 73 -

Example 52, is a control with anionic as the majority surfactant. Examples 53 and 54 show that when nonionic gum stabilizer (locust bean) is used, phase separation is prevented whereas when an anionic gum stabilizer (xanthan) is used, phase separation is still close to the control. Example 56 shows that the anionic ratio can be changed from 13:2 to 9:6 without phase separation. Conversely, Example 56 is a control with amphoteric as the majority surfactant. Examples 57 and 58 show that when an anionic gum stabilizer (xanthan) is used, phase separation is prevented whereas when a nonionic gum stabilizer (locust bean) is used, phase separation is still close to the control. Example 59 shows that the amphoteric ratio can be changed from 11:4 to 7.5:7.5 without phase separation.

These examples demonstrate the criticality that when the majority surfactant is anionic, that a nonionic gum stabilizer must be used. Furthermore, when the surfactant mixture is half or greater amphoteric, an anionic gum stabilizer must be used.

- 74 -

CLAIMS

1. A W_1 -O- W_2 multiple emulsion comprising:

(1) 1% to 99% by wt. of the composition of a W_1 /O emulsion comprising;

(a) 1% to 99% by wt. of the emulsion of an internal aqueous phase comprising (i) water; (ii) 0.01 to 30% by wt. emulsion solute; and (iii) 0-30% optional surfactant;

(b) 0.1% to 99% by wt. of the emulsion of an oil phase surrounding the internal aqueous phase wherein the oil is selected from volatile hydrocarbon, nonvolatile hydrocarbons, nonvolatile silicones and mixtures thereof;

(c) 0.1 to 20% by wt. of the emulsion of a surfactant emulsifier selected from silicon-free surfactant or surfactant blend having an HLB value of about 10 or less, an oil soluble silicon based surfactant, an oil-soluble polymeric surfactant and mixtures thereof; and

(d) a topically effective amount of a first topically active compound, which may be found in either the aqueous phase (a), oil phase (b) or both; and

(2) 1 to 99% by wt. of an external isotropic aqueous phase W_2 comprising:

(a) 2 to 80% by wt. aqueous phase of a surfactant phase which comprises a non-amido anionic or

- 75 -

nonionic or mixtures thereof in combination with at least one amphoteric; wherein the ratio of anionic and/or nonionic to amphoteric is 100:1 to 1:100

- 5 (b) optionally 0 to 60% by wt. of external phase of a second topically active compound; and
(c) optional solute.

2. A W_1 -O- W_2 multiple emulsion comprising:

- 10 (1) 1% to 99% by wt. of the composition of a W_1 /O emulsion comprising;
(a) 1% to 99% by wt. of the emulsion of an internal aqueous phase comprising (i) water; (ii) 0.01 to 30% by wt. emulsion solute; and
15 (iii) optional surfactant;
(b) 0.1% to 99% by wt. of the emulsion of an oil phase surrounding the internal aqueous phase wherein the oil is selected from volatile hydrocarbon, nonvolatile hydrocarbons,
20 nonvolatile silicones and mixtures thereof;
(c) 0.1 to 20% by wt. of the emulsion of a surfactant emulsifier selected from silicon-free surfactant or surfactant blend having an HLB value of about 10 or less, an oil soluble
25 silicon based surfactant, an oil-soluble polymeric surfactant and mixtures thereof; and
(d) a topically effective amount of a first topically active compound, which may be found

- 76 -

in either the aqueous phase (a), oil phase (b) or both; and

(2) 1 to 99% by wt. of an external isotropic aqueous phase W_2 comprising:

(a) 2 to 80% by wt. aqueous phase of a surfactant phase which comprises a non-amido anionic, or an amphoteric or a mixture of the two in which either (i) 60% by weight or greater is the anionic surfactant or (ii) 50% by weight or greater is the amphoteric surfactant;

(b) 0 to 60% by wt. of external phase of a second topically active compound;

(c) optional solute; and

(d) 0.01 to 10% of a nonionic natural gum stabilizer when 60% or greater of the surfactant phase in (2)(a)(i) above is anionic, or 0.01 to 10% of an anionic natural gum stabilizer when 50% or greater of the surfactant phase in (2)(a)(ii) above is amphoteric, wherein in both instances the multiple emulsion droplets maintain their integrity and the multiple emulsion composition does not phase separate.

3. An emulsion according to claim 1 or claim 2 comprising 2 to 90% by wt. $W_1/0$ emulsion.

4. An emulsion according to claim 3, comprising 5 to 80% by wt. $W_1/0$ emulsion.

- 77 -

5. An emulsion according to any of the preceding claims,
wherein the solute in the internal aqueous phase is
alkali metal chloride, sucrose or glucose.
- 5 6. An emulsion according to any of the preceding claims
wherein the oil phase comprises 1 to 80% of the
internal W₁/O phase.
- 10 7. An emulsion according to any of the preceding claims
wherein the hydrocarbon is a saturated vegetable based
oil.
- 15 8. An emulsion according to claim 7, wherein oil is > 50%
saturated.
9. An emulsion according to claim 8, wherein oil is > 85%
saturated.
- 20 10. An emulsion according to any of the preceding claims
wherein the emulsifier (c) is cetyl dimethicone
copolyol.
- 25 11. An emulsion according to any of the preceding claims
wherein the topically active compound (1)(d) is lactic
acid.
12. An emulsion according to claim 10, wherein the second
topically active compound (2)(b) is also lactic acid.

- 78 -

13. An emulsion according to any of the preceding claims wherein topically active compound is a nonionic hair styling polymer.

5

14. An emulsion according to any of the preceding claims wherein topically active compound is PVP.

15. An emulsion according to any of the preceding claims,
10 which is stable at a temperature of 25°C after 2 weeks.

16. An emulsion according to claim 15, which is stable after 30 days.

15 (e) 17. An emulsion according to any of the preceding claims, wherein the natural gum stabilizing polymer is locust bean gum or guar gum.

1/2

Fig.1A.

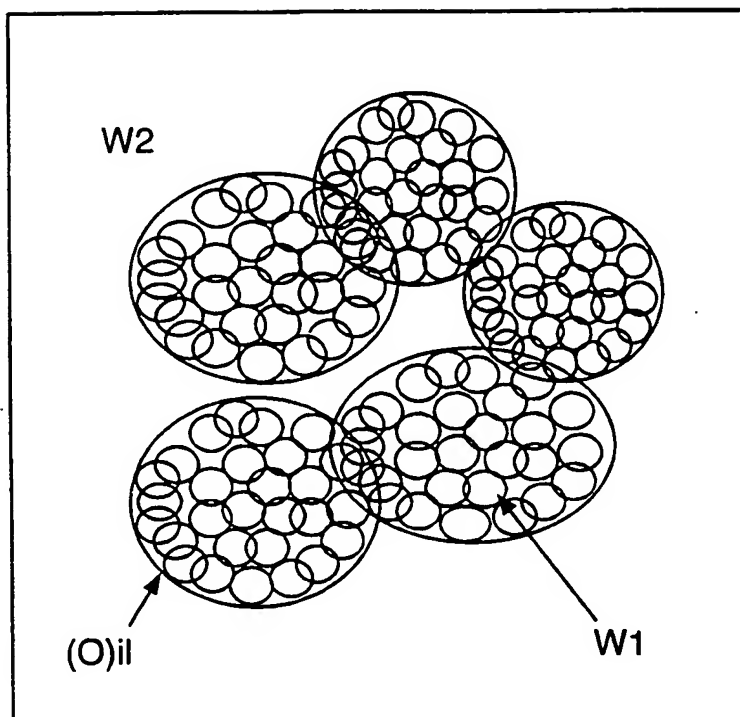
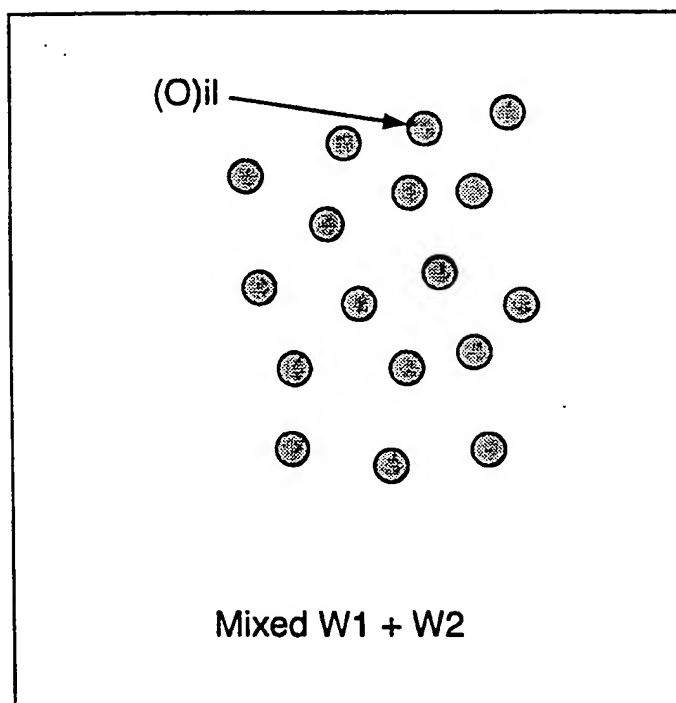


Fig.1B.



2/2

Fig.2. Addition of anionic natural gum polymer to amphoteric surfactant gives a gelled external (W2) phase

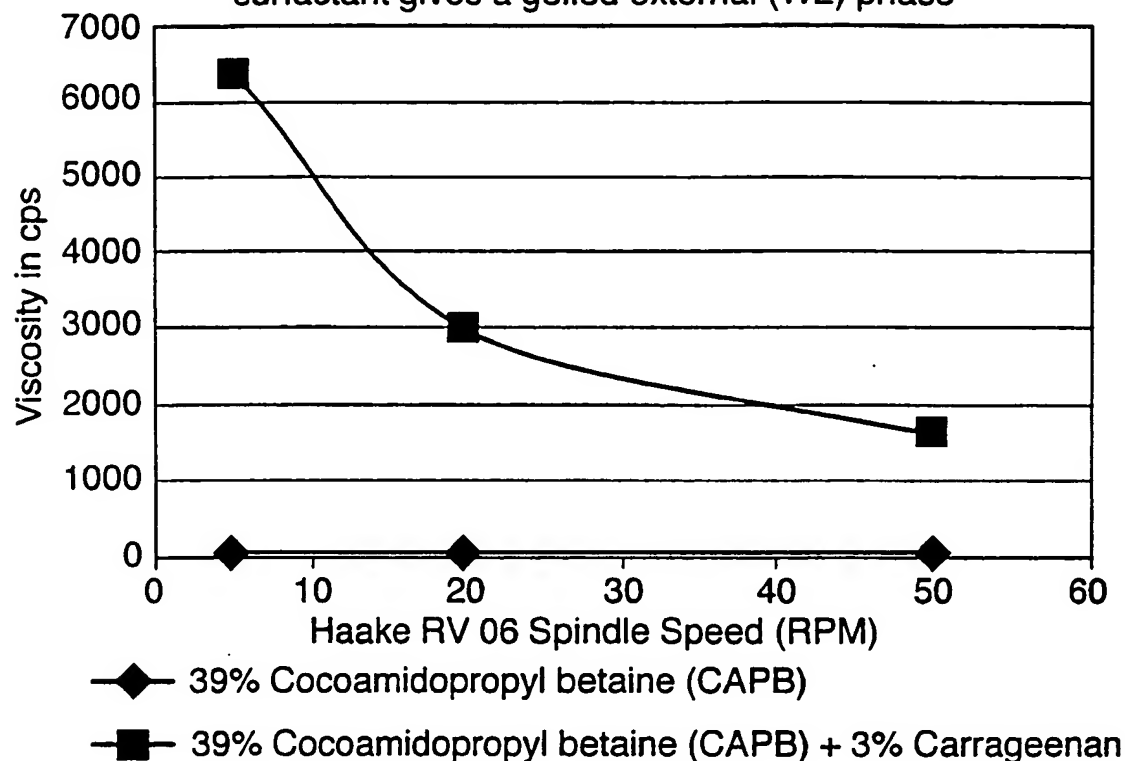
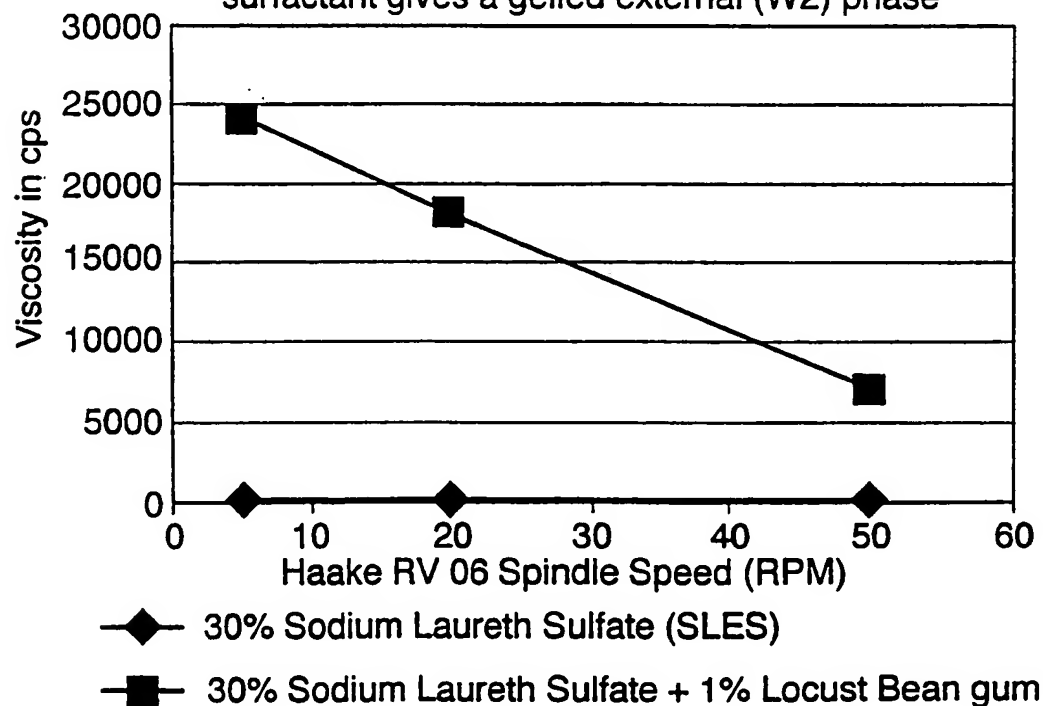


Fig.3. Addition of nonionic natural gum polymer to anionic surfactant gives a gelled external (W2) phase



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/10378

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 908 170 A (I. AFRIAT ET AL) 14 April 1999 (1999-04-14) claim 1	1
A	US 4 254 105 A (H. FUKUDA) 3 March 1981 (1981-03-03) claim 1; example 10	1
A	US 5 656 263 A (A. FRUCTUS) 12 August 1997 (1997-08-12) cited in the application the whole document	1
A	US 5 306 498 A (L. VESPERINI ET AL.) 26 April 1994 (1994-04-26) cited in the application claim 1	1
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 February 2001

Date of mailing of the international search report

23/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Glikman, J-F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/10378

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 332 595 A (A. GAONKAR) 26 July 1994 (1994-07-26) cited in the application table II	1
A	US 4 083 798 A (J. VERSTEEG) 11 April 1978 (1978-04-11) cited in the application claim 1	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/10378

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 908170	A	14-04-1999	FR 2769224 A	09-04-1999
			AT 193437 T	15-06-2000
			BR 9804154 A	28-03-2000
			CA 2246583 A	03-04-1999
			DE 69800169 D	06-07-2000
			DE 69800169 T	28-09-2000
			ES 2149039 T	16-10-2000
			JP 3011696 B	21-02-2000
			JP 11180824 A	06-07-1999
			PL 328936 A	12-04-1999
			US 6149900 A	21-11-2000
<hr/>				
US 4254105	A	03-03-1981	JP 53031578 A	24-03-1978
			JP 58006530 B	04-02-1983
			JP 1117081 C	15-10-1982
			JP 52046382 A	13-04-1977
			JP 55023087 B	20-06-1980
			FR 2326914 A	06-05-1977
			GB 1541463 A	28-02-1979
<hr/>				
US 5656263	A	12-08-1997	FR 2702391 A	16-09-1994
			US 5958435 A	28-09-1999
			AT 172109 T	15-10-1998
			CA 2118761 A	12-09-1994
			DE 69413867 D	19-11-1998
			DE 69413867 T	08-04-1999
			DK 614660 T	23-06-1999
			EP 0614660 A	14-09-1994
			ES 2122181 T	16-12-1998
			US 5576064 A	19-11-1996
<hr/>				
US 5306498	A	26-04-1994	FR 2681246 A	19-03-1993
			AT 119032 T	15-03-1995
			CA 2065219 A	06-10-1992
			DE 69201504 D	06-04-1995
			DE 69201504 T	29-06-1995
			DK 507693 T	26-06-1995
			EP 0507693 A	07-10-1992
			ES 2069389 T	01-05-1995
			JP 5112425 A	07-05-1993
<hr/>				
US 5332595	A	26-07-1994	NONE	
<hr/>				
US 4083798	A	11-04-1978	NONE	
<hr/>				